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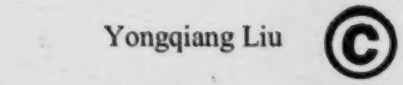
Flotation Separation of Carbonate from Sulfide Minerals

by

Yongqiang Liu 

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the Degree of ***Master of Science***

in

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Abstract

This research work was carried out with the objective of removing carbonate minerals from refractory gold-bearing sulfide ores by froth flotation. Small scale flotation tests were conducted on representative single minerals of carbonate and sulfide such as calcite, dolomite, pyrite, chalcopyrite, and their mixtures. It was found that the carbonate minerals could be floated from the sulfide using sodium oleate as a collector and a mixture of thioglycollic acid (TGA) and citric acid (CA) as a depressant. The mechanism by which the flotation reagents functioned was investigated using solution chemistry, electrokinetic potential, and Fourier transform infrared spectroscopic (FTIR) studies. The results indicated that the depressant (TGA) did not affect the adsorption of sodium oleate on carbonate minerals. However, TGA adsorbed on chalcopyrite through chemisorption, which prevented the adsorption of sodium oleate on the chalcopyrite surface. On the other hand, TGA reacted and removed lattice iron ionic species from pyrite surfaces thus creating an electrostatic repulsion between the surface and the oleate anions. The addition of citric acid improved the depressive function of TGA because it inhibited metal ions that could catalyze the oxidation of TGA. The process developed could potentially be used to float carbonate minerals from refractory gold-bearing sulfide ores prior to pressure oxidation, improving the efficiencies of the pressure oxidation – cyanidation processes.

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1 INTRODUCTION

The work described in this thesis is part of a comprehensive research program aimed at improving the efficiency of the pressure oxidation-cyanidation technology for the extraction of gold from refractory gold-bearing sulfide ores. The following provides background information for the research work.

1.1 Refractory gold ores

1.1.1 Gold minerals and gold-bearing minerals

There are very few naturally occurring compounds of gold due to its inert properties at ambient temperatures and pressures. Gold occurs mainly in its native form, as alloys with silver, or to a lesser degree, as gold compounds with tellurium and antimony. Gold and gold minerals are always contained within other minerals such as sulfide, silicate, carbonate and oxide either as very small inclusions or as ionic substitutions (Boyle, 1979; Paterson, 1990; Stanley, 1987). The most common gold minerals are listed in Table 1 and the most common gold-bearing sulfide minerals are listed in Table 2.

Table 1 List of the most common gold minerals (Marsden and House, 1992)

	Native gold	Electrum	Calaverite	Sylvanite	Aurostibite	Maldonite
Formula	Au	(Au, Ag)	$AuTe_2$	Au_2AgTe_4	$AuSb_2$	Au_2Bi
Au, %	>75	45-75	39.2-42.8	24.2-29.9	43.5-50.0	64.5-65.1

Table 2 List of the most common gold-bearing sulfide minerals

	Pyrite	Arsenopyrite	Stibnite	Chalcopyrite	pyrrhotite
Formula	FeS_2	FeAsS	Sb_2S_3	$CuFeS_2$	$Fe_{(1-x)}S$

1.1.2 Refractoriness of gold ores

In the traditional gold extraction circuits, there are three main unit processes involving crushing and grinding, cyanidation, and precipitation, as shown in Figure 1.

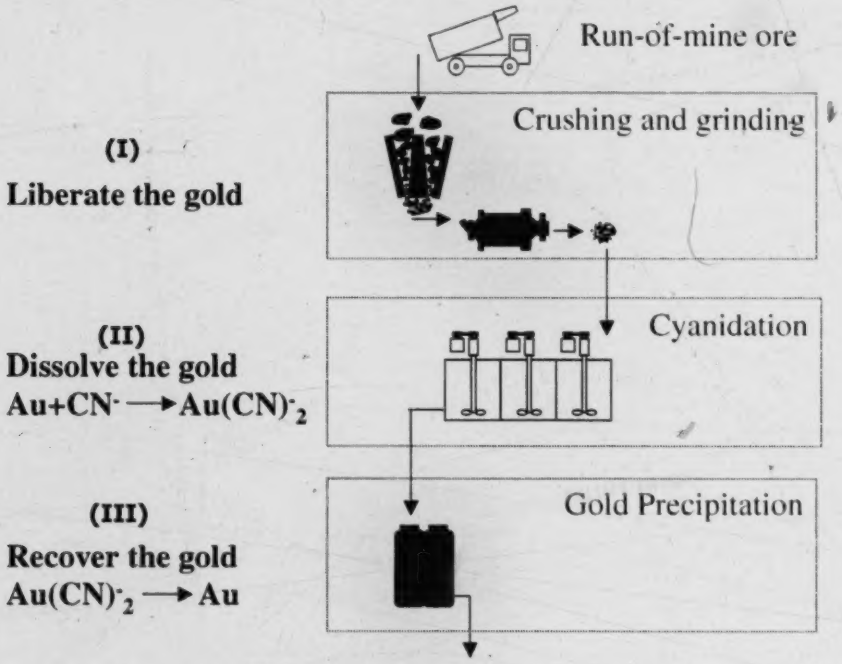


Figure 1 Major process steps in gold extraction

According to the degree of gold extraction by direct cyanidation, gold ores can be classified as "free milling", "complex" or "refractory" (La Brooy et al., 1994). In this classification, "free milling" refers to the gold ores from which more than 90% of the gold can be extracted after a 20-30 hour conventional cyanidation leach; "refractory" refers to the gold ores from which very low gold recovery is obtained after the conventional cyanidation with enhanced reagent addition, and "complex" refers to the gold ores whose gold recovery is economically acceptable after the conventional cyanidation with significantly higher cyanide or oxygen addition. This classification is summarized in Table 3.

Table 3 Classification of gold ore refractoriness (La Brooy et al., 1994)

Category	Degree of refractoriness	Recovery of gold with conventional cyanidation
Refractory ore	Highly refractory	<50%
	Moderately refractory	50-80%
Complex ore	Mildly refractory	80-90%
Free Milling ore	Non refractory	90-100%

1.1.3 Reasons for the refractoriness of gold ores

The refractoriness of gold ores may result from the following reasons:

- Gold is encapsulated in a sulfide mineral matrix or occurs in submicroscopic form either finely disseminated or in solid solution with the sulfide, as can be seen in Figure 2. In this case, even fine grinding fails to open sufficient channels for cyanide solutions (Demopoulos and Papangelakis, 1989; Iglesias and Carranza, 1994; Komnitsas and Pooley, 1989; La Brooy et al., 1994; Lehmann et al., 2000; Marsden and House, 1992). Complete sulfide preoxidation is necessary to render the gold amenable to high levels of recovery by cyanidation (Weir et al., 1986).

- Oxygen and cyanide that are vital to gold dissolution are significantly consumed by the constituent reactive minerals in side reactions. For example, the presence of intermediate species, such as thiosulphates and arsenites consume oxygen so that there may be insufficient oxygen in the pulp to leach the gold (Iglesias and Carranza, 1994; Komnitsas and Pooley, 1989), and the presence of certain sulfide minerals which decompose to form cyanicides will combine with and deplete cyanide available to dissolve gold (Komnitsas and Pooley, 1989).

- The dissolved gold-cyanide complex may be adsorbed or re-precipitated by components of the ore so that gold is lost from the leach liquor (Iglesias and Carranza, 1994; Komnitsas and Pooley, 1989; La Brooy et al., 1994; Lehmann et al., 2000). This phenomenon is generally referred to as "preg-robbing".

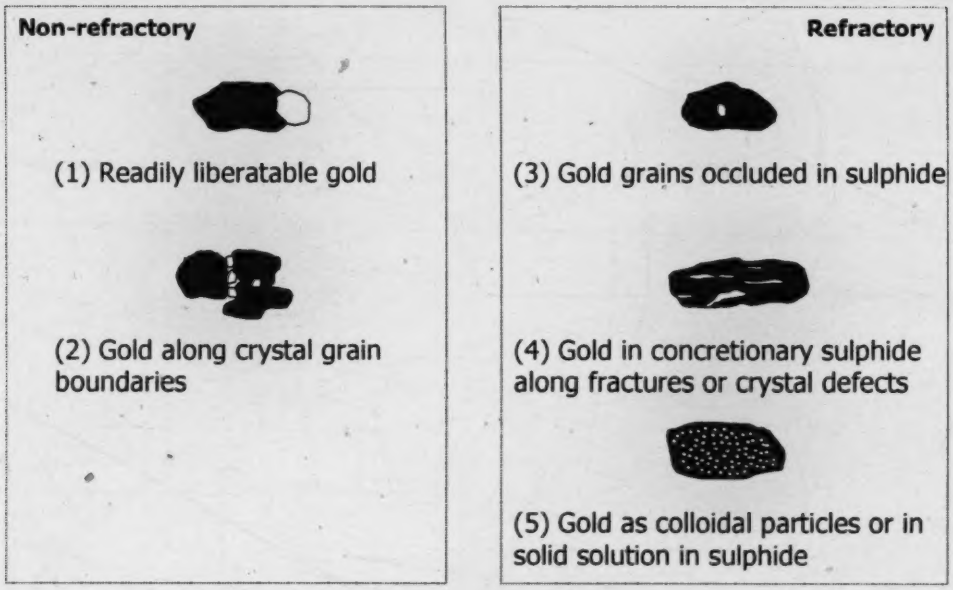

Non-refractory
(1) Readily liberatable gold
(2) Gold along crystal grain boundaries
Refractory
(3) Gold grains occluded in sulphide
(4) Gold in concretionary sulphide along fractures or crystal defects
(5) Gold as colloidal particles or in solid solution in sulphide

Figure 2 Gold associations with sulfide minerals

1.2 Pretreatment of refractory gold ores

Most of the gold ore deposits being explored or developed are highly or moderately refractory (Berezowsky and Weir, 1984; Fraser et al., 1991). Gold production will be increasingly dependent upon the efficient treatment of these refractory ores that do not provide economic gold recovery by direct cyanide leaching. Therefore, a significant amount of effort has been directed at the treatment of the refractory ores since the 1970s (Marsden and House, 1992).

In order to recover gold from these refractory gold ores, an oxidative pretreatment is required to destruct the host sulfide minerals so that the encapsulated gold is released and becomes amenable to the subsequent cyanide leaching. Generally, pretreatment includes roasting, pressure oxidation, biological oxidation or chemical oxidation, as illustrated in Figure 3. To date, chemical oxidation, including the Artech/Cashman Process, the Redox/Nitrox Processes, the Actvox Process, etc., is mostly being tested on the

laboratory scale. Roasting and pressure oxidation have been successfully used on a commercial scale, while biological oxidation has been applied on a small scale.

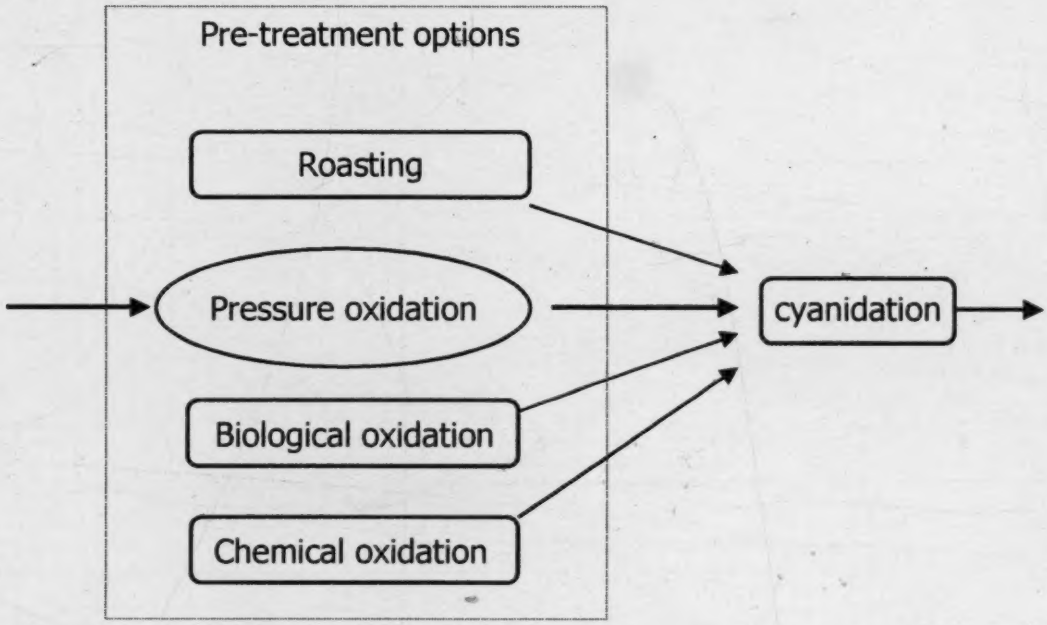


Figure 3 Pretreatment options for refractory gold ores

1.2.1 Roasting

Roasting has been used to treat refractory gold ores and concentrates for more than 100 years (Fraser et al., 1994; Marsden and House, 1992). The traditional roasting was carried out in fixed bed hearth, rotary furnace or stationary fluid bed. Some important technical innovations, such as the Circulating Fluid Bed Roaster and the Oxygen Enriched Roasting Process, have made it possible to treat the whole ore of refractory ores without the need of preconcentration.

Pyrite roasting converts pyrite in stages at a temperature of 650-700°C to hematite that is insoluble in cyanide solution and sufficiently porous to expose the gold particles. The conversion reactions are:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \qquad (1.)$$

$$2FeAsS + 5O_2 \rightarrow Fe_2O_3 + As_2O_3 + 2SO_2 \quad (2.)$$

This process produces pollutants such as sulfur dioxide and arsenic trioxide that need to be removed before discharge. Stringent discharge standards make roasting very expensive. In addition, localized high temperatures during roasting may produce impervious, glassy fluxes that encapsulate the gold and reduce gold extraction (Fraser et al., 1991; Komnitsas and Pooley, 1989). In fact, the available data suggests that the recovery of gold following a roasting pretreatment is generally lower than that after a pretreatment by pressure oxidation (Fraser et al., 1991; Lehmann et al., 2000). Therefore, roasting pretreatment is gradually being replaced by pressure oxidation or biological oxidation.

1.2.2 Biological oxidation (Biooxidation)

Biological oxidation is a process in which the oxidation of sulfide minerals is catalyzed by microorganisms such as thiobacillus, sulfolobus and acidianus (Ubaldini et al., 2000; van Aswegen and Marais, 1999). The sulphur species and ferrous iron are oxidized to sulphate and ferric iron respectively. Thiobacillus derives carbon from carbon dioxide and energy from ferrous iron and reduced sulphur species at pH of 1-3.5 and a temperature of 20-40°C. Sulfolobus and acidianus can obtain carbon from both organic and inorganic compounds and the sources of energy for their growth are reduced sulphur species and ferrous iron. Sulpolobus grows at pH 1-6 and at temperatures of 50-90°C, and acidianus grows at pH 1-3 and temperatures of 45-70°C (Iglesias and Carranza, 1994; Ubaldini, 2000; van Aswegen and Marais, 1999).

Biological oxidation can be direct and/or indirect:

- Direct biological oxidation:

$$4FeS_2 + 15O_2 + 2H_2O \xrightarrow{bacteria} 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad (3.)$$

$$4FeAsS + 13O_2 + 6H_2O \xrightarrow{bacteria} 4H_3AsO_4 + 4FeSO_4 \quad (4.)$$

- Indirect biological oxidation:

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S^o \quad (5.)$$

$$2FeAsS + 2Fe_2(SO_4)_3 + 5/2O_2 + 3H_2O \rightarrow 2H_3AsO_4 + 6FeSO_4 + 2S^o \quad (6.)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \xrightarrow{bacteria} 2Fe_2(SO_4)_3 + 2H_2O \quad (7.)$$

$$2S^o + 2H_2O + 3O_2 \xrightarrow{bacteria} 2H_2SO_4 \quad (8.)$$

After a long period of study, a demonstration plant was first built at the Fairview Mine in South Africa in 1988, which treated a gold-bearing arsenopyrite concentrate at a rate of 10 t/day (Haines, 1986; van Aswegen and Marais, 2000). This plant was expanded in 1991 to the capacity of 35 t/day. A second plant was built at the Sao Bento Mine in Brazil in 1990/1991. A third plant, the Harbor Lights gold mine at Leonora in Western Australia, processed arsenopyritic concentrates at the rate of 40 ton/day from June 1992 to 1994 (Barter et al., 1992; van Aswegen and Marais, 1999).

Major advantages of biooxidation are low environmental pollution, low temperature and pressure, low degree of process control, and possibility to control the extent of sulfide oxidation. However, biooxidation usually requires long residence time, careful temperature control, and it results in a low degree of arsenic precipitation during the oxidation process. Due to these reasons it is generally used to treat flotation concentrates and is run only at pilot and small commercial scales (Fraser, et al., 1991; La Brooy et al., 1994; Nieves and Carranza, 1994).

1.2.3 Pressure oxidation

Pressure oxidation can be conducted either in an acid or an alkaline medium. Predominantly, pressure oxidation is carried out in acid medium. Acid pressure oxidation is generally conducted at temperatures of 170-225°C and pressures of 1100-3200 kPa with a retention time of 1-3 hours in four or five compartment autoclaves (Berezowsky et al., 1991; La Brooy et al., 1994). Oxygen mass transfer to mineral surfaces is an important factor to control the rate of reaction. Higher oxygen partial pressure is necessary to allow more rapid oxidation. Typical oxygen utilization efficiency is 50-90%, which is dependent on the amount of CO_2 in the autoclave. Pulp acidity is generally controlled at pH <2 to maintain a satisfactory redox potential and prevent excessive precipitation in the autoclaves.

The process chemistry of acid oxidation of arsenopyrite and pyrite is as follows (Berezowsky and Weir, 1984):

- Sulfide sulfur is oxidized to sulfate:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (9.)$$

$$4FeAsS + 11O_2 + 2H_2O \rightarrow 4HAsO_2 + 4FeSO_4 \quad (10.)$$

- The divalent iron and trivalent arsenic are oxidized to their respective ferric and arsenate states:

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad (11.)$$

$$2HAsO_2 + O_2 + 2H_2O \rightarrow 2H_3AsO_4 \quad (12.)$$

- In the presence of relatively large amounts of sulfuric acid and ferric sulfate, elemental sulfur may be formed in the lower temperature range of 100-160°C:

$$FeS_2 + 2O_2 \rightarrow FeSO_4 + S^o \quad (13.)$$

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S^o \quad (14.)$$

$$4FeAsS + 5O_2 + 4H_2SO_4 \rightarrow 4HAsO_2 + 4FeSO_4 + 4S^o + 2H_2O \quad (15.)$$

$$2FeAsS + 7Fe_2(SO_4)_3 + 8H_2O \rightarrow 2H_3AsO_4 + 16FeSO_4 + 2S^o + 5H_2SO_4 \quad (16.)$$

Formation of elemental sulphur is undesirable because it will occlude un-reacted sulfides so as to hinder or prevent their complete oxidation, occlude gold particles so as to hinder or prevent their extraction during cyanidation, and increase cyanide and oxygen consumption during cyanidation. Sulphur oxidation is, therefore, conducted at temperatures in excess of 160°C to promote the complete oxidation of sulfides to sulfates

$$S^o + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad (17.)$$

- Arsenic is precipitated as ferric arsenate thus avoiding the additional isolation process:

$$Fe_2(SO_4)_3 + 2H_3AsO_4 \rightarrow 2FeAsO_4 + 3H_2SO_4 \quad (18.)$$

- Some of the ferric sulfate can be hydrolyzed and precipitated as hematite, or as a basic ferric sulfate:

$$Fe_2(SO_4)_3 + 3H_2O \rightarrow Fe_2O_3 + 3H_2SO_4 \quad (19.)$$

$$Fe_2(SO_4)_3 + 2H_2O \rightarrow 2Fe(OH)SO_4 + H_2SO_4 \quad (20.)$$

$$3Fe_2(SO_4)_3 + 14H_2O \rightarrow 2H_3OFe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \quad (21.)$$

$$Fe_2(SO_4)_3 + 2H_3AsO_4 + 2H_2O \rightarrow 2FeAsO_4 \cdot H_2O + 3H_2SO_4 \quad (22.)$$

Pressure oxidation offers a number of advantages over roasting and biological oxidation. Compared to biological oxidation, pressure oxidation needs a very short residence time and is a commercially proven, effective process. Compared to roasting, it can precipitate most of the arsenic within the oxidation steps, and does not emit harmful gases and particulates such as SO_2 and As_2O_3. In addition, high recovery of gold can be achieved due to the high degree of oxidation of sulfide. Presently, pressure oxidation appears to be the best established approach to the pretreatment of refractory gold ores with sufficient grades (Demopoulos and Papangelakis, 1989; Fraser et al., 1991).

1.3 Difficulties in pretreatment of high carbonate refractory gold ores

Due to the characteristic of gold ore formation, gold ores are always accompanied with carbonate minerals (Marsden and House, 1992). When a refractory gold ore has high carbonate content, roasting is seldom used because of pollution and low gold recovery. Biological oxidation is not suitable because the presence of carbonate influences the acid requirement for maintaining the correct pH (O'Connor and Dunne, 1994). As already mentioned (section 1.2.2), the biological process utilizes a mixed population of bacteria to break down the sulfide matrix. Most bacteria grow in the low pH range, and different

bacteria have different optimum pH values; therefore, it is necessary to control the pH within low and narrow ranges to maintain the right balance of bacterial species to optimize the rate of oxidation (van Aswegen and Marais, 1999).

When a refractory gold ore has a high carbonate content, direct acid pressure oxidation is problematic because the carbonate minerals consume large amount of acid, and this not only adversely affects the economics of the process, but also lowers the pressure oxidation efficiency due to the release of CO_2 gas that takes up space inside the autoclave and excludes oxygen from the system (Fraser et al., 1991). For example, oxygen utilization is less than 75% when refractory gold ores contain 6% to 8% CO_2 (as carbonate) (Weir et al., 1986). Even if the refractory gold-bearing sulfide ores generate sufficient acid during the pressure oxidation process that can be recycled to neutralize the carbonate before it enters the autoclave, the slimy precipitates formed from the neutralization reactions can foul the activated carbon in the gold recovery processes. The mass of hydroxides, hydrated oxides and gypsum precipitated from the slurry changes the slurry viscosity and can have a substantial impact on downstream processing (Fraser et al., 1991).

Alkaline pressure oxidation was proposed specifically to process refractory gold ores with high carbonate content. However, the process has several disadvantages which prevent it from being used extensively: (1) alkaline pressure oxidation is operated under neutral or slightly alkaline conditions, and thus sulfur and arsenic in the refractory ores are completely dissolved as sulfates and arsenates, making the isolation of arsenic very difficult (Demopoulos and Papangelakis, 1989); (2) insoluble iron oxides and hydroxides form under alkaline leach conditions and coat gold and sulfide minerals, resulting in low gold recovery (La Brooy et al., 1994; Thomas, 1991); (3) the costs of reagents are high and to be economic, it is generally required that the sulfide sulfur contents in the ores are below 2% (Wicks, 1987). To date, this method is used only in Barrick's Mercur plant in Utah, USA.

Currently, there is no appropriate process to treat refractory gold ores with high carbonate contents. Pre-concentration by flotation before either bacterial oxidation or

pressure leaching is a possible process route to treat this type of ores (see Figure 4). However, no data are available in the technical literature.

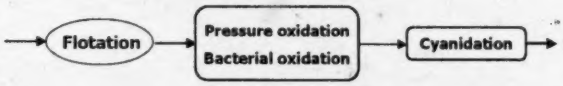


Figure 4 Flowsheet options for refractory gold ores with high carbonate

1.4 Flotation as a pre-concentration technique in gold ore processing

The purpose of pre-concentration is to (1) produce a high grade gold concentrate for more economic subsequent treatment, and/or (2) to reject a portion of the ore that is barren but which would otherwise adversely affect subsequent gold extraction, e.g., cyanide consuming sulfides, gold adsorbing carbonaceous matter and acid consuming carbonates (Marsden and House, 1992). Flotation has been the most common pre-concentration operation in gold ore processing.

1.4.1 Bulk flotation to produce a gold-rich concentrate

- **Flotation of native gold**

Native gold particles are naturally floatable. This may be caused by the variation in composition (Allan and Woodcock, 2001), surface contamination of organics (Dunne, 1991; Wang and Poling, 1983) or the variations in flotation pulp potential (Aksoy and Yarar, 1989). Untarnished gold of the appropriate size can be readily floated with only a frother (Dunne, 1991; Wang and Poling, 1983) by the use of oxygen or nitrogen (Hintikka and Leppinen, 1995).

Xanthates are the most common collectors for the flotation of native gold, gold minerals and gold-bearing sulfides although it was suggested recently that water-insoluble oily collectors are the best collectors for native gold (Klimpel, 1999). Among the various explanations, electrochemical reactions are the most convincing mechanism of how the reagents form hydrophobic coatings on gold (Woods, 1984). By this

mechanism, a xanthate ion diffusing from bulk solution to the surface of the gold undergoes an anodic reaction in which xanthate ion is discharged and an electron is released into the gold. The xanthate is thus chemisorbed onto the gold surface. The non-polar group of xanthate directs towards the solution phase, thus giving a hydrophobic surface condition. At the same time, dissolved oxygen diffusing from bulk solution to the gold surface undergoes a two stage cathodic reaction by which water molecules and the electrons generated in the anodic reaction produce hydroxyl ions. In addition, xanthate ions can be electrochemically oxidized to dixanthogen under oxidizing conditions. The dixanthogen formed at the surface of gold also contributes to the hydrophobic coatings.

Dithiophosphates (DTP) are used as adjunct or secondary collectors to xanthate. It is reported that they go through the similar reactions to those for xanthate, and form di-thiophosphogen compounds (Basilio et al., 1991). Mercaptobenzothiazole (MBT), thionocarbamate, and thiocarbanilide are also used as promoters but their functions are not well understood (Allan and Woodcock, 2001; Klimpel, 1999). Occasionally, amines are used to float gold as well (O'Connor and Dunne, 1991; Ramsay, 1978).

Teague et al. (1998, 1999) studied the flotation behavior of free gold and refractory gold under the same conditions within the same pulp. They claimed that the flotation recovery of free gold was largely affected by physical constraints like the shape and size of the particles, the degree of water and gangue transport to the froth, the stability of the froth, and the extent of bubble loading of sulfide particles. The flotation of refractory gold followed a similar trend to the recovery of refractory pyrite and pyrrhotite and was mainly affected by chemical conditions in the pulp such as redox potential, aeration conditions, copper activation, reagent synergism and galvanic interaction. Teague et al. (2000) reported that when copper sulphate was added after the collector, the recovery of free gold increased dramatically so that there was an overall increase in total gold recovery of up to 6% compared with the usual sequence of adding the copper first because the copper sulphate made the froth stable and the copper ions did not have the opportunity to exchange ions with iron sulfide surfaces when added after the collector (i.e., immediately prior to the start of flotation).

- **Flotation of gold-bearing iron sulfide minerals**

Pyrite, arsenopyrite and pyrrhotite are the most common gold-bearing sulfide minerals, which are usually floated by thiol collectors. The mechanism of adsorption of xanthates on pyrite surfaces has been extensively studied and was found similar to that on gold. Recently, collectors such as dithiocarbamates and thionocarbamates and mixtures of them with xanthates and mercaptobenzothiazoles have been used to float sulfides (Chryssoulis, 1990). Amine based collectors have been used to float cyanided pyrite from cyanidation residues without the use of acid preconditioning (O'Connor and Dune, 1994). Thionocarbamates, thiocarbamates and thioureas have been found to be stable over a wide pH range. It was also reported that the addition of hydrolyzed polyarylamide reduced the nonproductive consumption of butyl xanthate when floating gold-bearing pyrite (Orel et al., 1986).

Copper sulphate was often used as an activator for iron sulfide flotation (O'Connor, 1990; Teague et al., 2000) and various depressants were added to depress the gangue (Da Silva, et al., 1989; Steenberg, 1984). Lignin sulphonate has been shown to be an efficient depressant for carbonate (O'Connor and Dunne, 1994).

- **Flotation of gold-bearing copper sulfide minerals**

Because copper-gold ores contain small quantities of gold and many reagents used to depress sphalerite in the differential flotation of Cu-Pb-Zn ores also depress native gold, it is preferable to float the gold into a copper concentrate (Bulatovic, 1997; O'Connor and Dunne, 1994). This flotation is carried out using xanthate and a promoter, and Na_2S is always added (Clarke and Beerman, 1985; Oudene and De Cuyer, 1986). It was reported that Aero 7249 Promoter (a monothiophosphate) could increase the recovery of native gold (Hartati et al., 1997) and improve the selectivity of gold against the sulfides (Forrest et al., 2001).

Since copper-gold flotation emphasizes maintaining high grade copper concentrates, the recovery of gold is not optimum under these conditions (Bulatovic, 1997). Combinations of xanthate and dithiophosphate as collectors can give satisfactory results

with respect to the concentrate grade of copper and gold recovery. Citric acid and oxalic acid can improve gold recovery due to the possible effect of surface cleaning by removing iron stains and iron oxide/hydroxide films.

1.4.2 Differential flotation to separate gold-bearing minerals from gold-barren gangue

Since gold ores consists of mixtures of gold, gold bearing sulfides and so on, a differential flotation is often necessary to separate gold or gold bearing minerals from other gold-barren minerals that may have adverse affects on the subsequent gold recovery processes.

- **Separation of Gold from pyrite**

Flotation selectivity of gold against pyrite can be enhanced using alkoxy or phenoxy carbonyl alkyl thionocarbamates and thioureas, dialkyl or diaryl monthiophosphates and monothiophosphinates, glyoxalidine and aminothiophenols (Marabini et al., 1991; Nagaraj and Avotins, 1988). Gold flotation can be depressed by sulfide and ferric ions (Aksoy and Yarar, 1989). Monte et al. (1997) studied the selective flotation of gold from pyrite under oxidizing conditions, and their results showed that a high selectivity for gold from pyrite could be obtained at pH higher than 10. Hydrogen peroxide could clean the surface of gold, rendering it very hydrophilic but not blocking the adsorption of xanthate. At the same time, the pyrite surface was completely oxidized and not amenable to flotation with xanthate.

- **Separation of pyrite from arsenopyrite**

In the pyrite-arsenopyrite system, gold is always associated with arsenopyrite (Kogan et al., 1985; Matis et al., 1992; Swash, 1988). Arsenopyrite was usually depressed and pyrite was floated on the basis of their floatability difference. More ideally in this system, the arsenopyrite was selectively floated from the pyrite to produce a concentrate for treatment by pressure oxidation or bacterial oxidation. Bacterial oxidation subsequent to flotation is, however, sensitive to the presence of residual flotation reagents and hence it is critical to establish the toxicity of the reagents prior to use.

Separation between pyrite and arsenopyrite was achieved by addition of oxidants or reductants to regulate the oxidation state of pyrite and arsenopyrite so as to give rise to the difference in floatability (Matis et al., 1992). Potassium permanganate was usually used as an oxidant and arsenopyrite was depressed by permanganate at a redox potential of between 400 and 500 mV (O'Connor and Dunne, 1994). Potassium peroxodisulphate was used not only to depress the arsenopyrite but also activate the pyrite (Kogan et al., 1985). In this separation, modifiers such as sodium metabisulphite, hydrazinium sulphate and magnesia were also added to improve the depression effect. Copper sulphate was also added to activate the target minerals. It was reported that using mixtures of dithiophosphates and dithiocarbamates, arsenopyrite could be floated from pyrite and the flotation recovery was 60% and 20%, respectively (O'Connor et al., 1990).

- **Separation of pyrrhotite from pyrite and /or arsenopyrite**

Pyrrhotite consumes a substantial amount of cyanide and oxygen in cyanide leaching and can be rejected by selective flotation of pyrite and arsenopyrite. Preaeration before flotation can depress pyrrhotite (Dunne, 1991). Conditioning with potassium permanganate in an alkaline circuit has also been tested. Dithiophosphates, usually used as a secondary collector, are selective against pyrite and to a lesser extent against arsenopyrite (O'Connor et al., 1990).

- **Separation of stibnite from pyrite and /or arsenopyrite**

When the gold bearing sulfide is accompanied by stibnite, the stibnite is often rejected by floating pyrite/arsenopyrite at a high pH, using hydroxide to depress the stibnite and copper sulphate to activate the arsenopyrite/pyrite (Orberbillig, 1964).

- **Separation of copper from pyrite, arsenopyrite, and /or pyrrhotite**

When copper-gold ores contain iron sulfide such as pyrite, arsenopyrite and pyrrhotite, the iron sulfide is usually depressed by the addition of cyanide and lime (or soda ash). Gold-bearing copper concentrate can be produced for smelting (O'Connor and Dunne, 1994).

1.5 Proposed reverse flotation of carbonate and depression of gold-bearing sulfide

From the forgoing description, it is seen that traditional gold ore flotation is mostly direct flotation of gold or gold-bearing sulfide minerals while rejecting the waste rock. However, the mineralogy of refractory gold ores is usually such that the gold-bearing sulfide minerals are finely disseminated or the gold is sub-micron in size, and thus gold loss to flotation tailings is significant. In this case, pre-concentration by flotation is not economic even though it has some cost savings achieved by removing deleterious material or by treating a smaller amount of materials. Therefore, when a gold ore has a high carbonate content and the gold and gold-bearing sulfide are finely disseminated, there is no effective process to recover the gold.

Therefore, we propose a reverse flotation process to remove carbonate from the gold ores as an alternative process option. It would involve recovering carbonate in the froth and keeping gold and gold-bearing sulfide in the tailings. The success of this process depends on: (1) selection of a suitable selective collector for carbonate flotation, and/or (2) selection of suitable depressants that can efficiently and selectively depress gold-bearing sulfide minerals. Note that depressants for the flotation of native gold particles are not essential since any native gold floated into the carbonate concentrate can be cyanide leached and recovered.

1.6 Advances in flotation of carbonate minerals

The most common and important carbonate mineral is calcite ($CaCO_3$), and to a lesser degree, dolomite ($CaMg(CO_3)_2$) and siderite ($FeCO_3$). The flotation of carbonate has been studied extensively.

1.6.1 Solubility of carbonate minerals

The carbonate minerals are moderately soluble in water due to their ionic bonding. The solubility of calcite and dolomite is in the order of 10^{-4} mol/L (Fuerstenau, 1985). The extent of dissolution of carbonate depends on the type of minerals and the concentration of chemicals in the solution. Under atmospheric condition, the dissolved

mineral species will undergo pH dependent hydrolysis and complexation reactions. For calcite, Ca^{2+} is predominant in acidic solution, while carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) are the predominant species in basic solution; for dolomite, Ca^{2+} and Mg^{2+} predominate below pH 10 while CO_3^{2-} and hydroxyl species of Ca and Mg are predominant above pH 10. Somasundaran et al. (1991) gave the species distribution diagram of calcite, as shown in Figure 5.

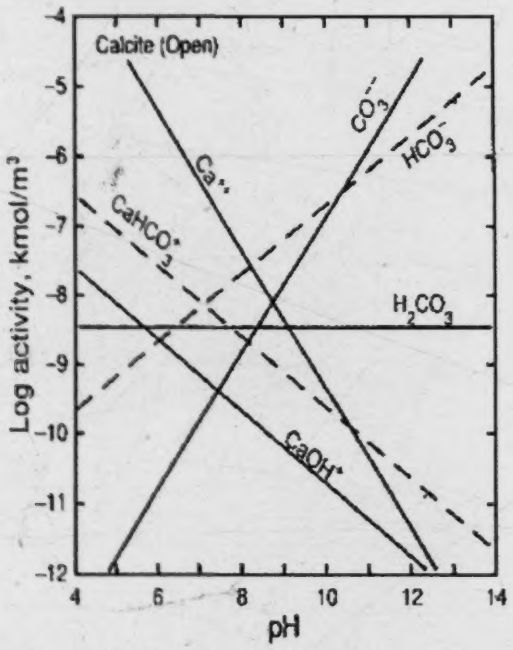


Figure 5 Species distribution diagrams for open systems of calcite (Somasundaran et al., 1991)

1.6.2 Flotation properties of carbonate

The flotation of carbonate such as calcite and dolomite has been studied by many researchers due to its industrial and theoretical importance. The flotation performance of carbonate varies greatly depending on pH, concentration and hydrocarbon chain length of collectors. The flotation of calcite increases with increase in pH and higher concentrations of collector are required to obtain the same approximate flotation response at a lower pH (Pugh and Stenius, 1985). Fuerstenau et al. (1967) studied the flotation

recovery of calcite with fatty acid as a collector (Figure 6). As can be seen, much higher concentration is required for a shorter-chain fatty acid to achieve the same flotation recovery.

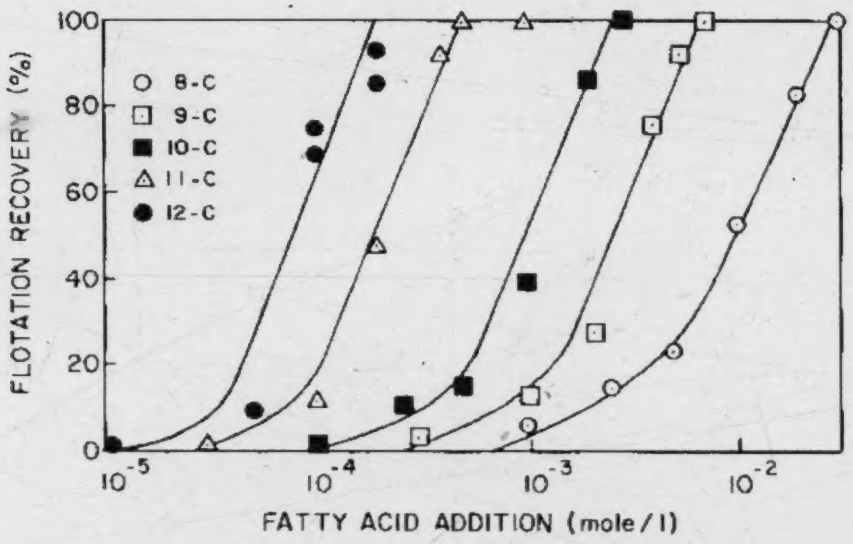


Figure 6 Floatability of calcite as a function fatty acid addition at pH 9.7

Flotation responses can be very different if the same carbonate mineral comes from different deposits (Sφrensen, 1973). This leads to the diverse opinions concerning the optimum conditions to attain maximum floatability of the carbonate.

1.6.3 Adsorption of collector on carbonate surfaces

1.6.3.1 Distribution of oleate species in aqueous solutions

Long chain fatty acids and their alkali salts, especially oleic acid and sodium oleate, are the most extensively used collectors for carbonate flotation (Pugh and Stenius, 1985). The oleate ionizes to form Ol^- at high pH, exists as neutral molecules (HOl) at low pH, and forms ion molecules complexes in the intermediate region (Somasundaran et al., 1991). Micellization or precipitation of the collector can take place in the solution when the collector concentration is high. Aggregates such as dimers (Ol_2^{2-}) can be formed in

pre-micellar solution. The distribution of oleate species as function of pH is shown in Figure 7 (Pugh and Steniu, 1985).

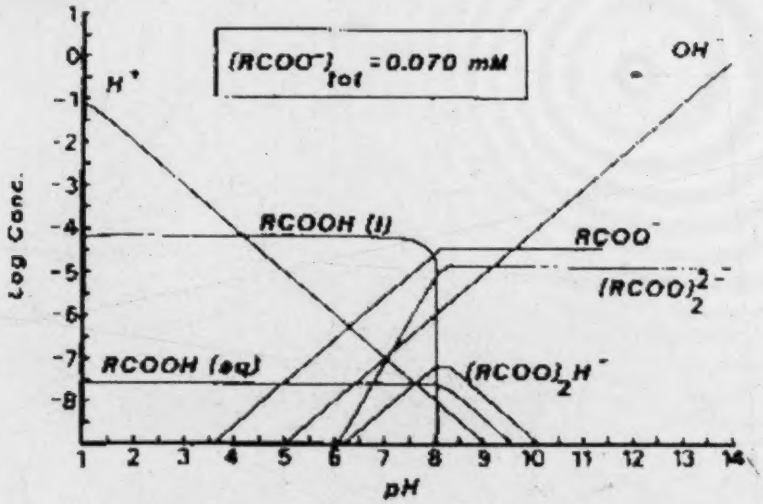


Figure 7 Distribution of oleate species as function of pH (Total oleate concentration: 0.07×10^{-3} mol/L)

Oleate has a low solubility in aqueous solutions and poor tolerance for multivalent cations. It was reported that these problems could be avoided by using mixtures of oleate and ethoxylated sulfonates (Xiao et al., 1989).

1.6.3.2 Adsorption of sodium oleate collector on mineral surfaces

The adsorption density of oleate at the surface of the particles that float is significantly greater than it is at the surface of those that do not. The extent of abstraction by calcite increases monotonically with the concentration of oleate in solution, showing no sign of leveling off or peaking within the limit of the experimental conditions up to 35 monolayers. The enthalpy of reaction is constant and close to the heat of formation of calcium oleate (Finkelstein, 1989).

Solution pH and temperature affect the adsorption of the collector on mineral surfaces. Data presented by Marinakis and Shergold (1985) showed that oleate adsorption on calcite was independent of pH between pH 9-12, whereas the data presented by

Cutierrez (1979) showed that a sharp maximum existed at about pH 10, followed by constant adsorption between pH 10.5 and 12. Higher solution temperature increased the adsorption in different regions of the adsorption curves (Hu et al., 1986).

The solution-phase calcium oleate can be converted to the adsorbed oleate. Giesekke and Harris (1984) studied the adsorption of oleate on calcite from a suspension of calcium oleate. They found that adsorption exceeded a nominal monolayer and yet was less than would have been adsorbed from an equivalent concentration of sodium oleate at the same temperature. The adsorption on the mineral increased markedly when the temperature was increased from 25 to 70°C. The degree of the adsorption was dependent on pH and calcium ion concentration. The form and size of the calcium oleate particles are also believed to be important factors in determining the extent of adsorption in this non-equilibrium system. Finkelstein (1989), on the other hand, believed that the efficiency of sodium oleate would be affected because it could be precipitated by dissolved calcium ions.

1.6.3.3 Mechanism of interaction of the collector and the mineral surfaces

The floatability of carbonate is related to the form of adsorbed collector on the mineral surface. The degree of floatability can be affected by the form of reagent at the mineral surface even though the adsorption products are intrinsically hydrophobic. For example, the floatability does not deteriorate when surface calcium oleate would be formed, which suggests that this species is effective in rendering the surface hydrophobic. However, its presence at mineral surfaces may reduce the floatability of particles if it enables bubbles to detach themselves from the particles although bulk calcium oleate is hydrophobic (Finkelstein, 1989). A major effort has been directed towards identification of the adsorbed oleate species as a distinct chemical entity (Giesekke, 1983; Miller and Keller, 1996); however, no absolute agreement has been reached. Miller and Keller (1996) claimed that the Ol^- was the effective ion in adsorption.

On the surface of minerals, there may exist different soluble species of oleate. In the review by Somasundaran et al. (1991), it is summarized that: in the low concentration region, the oleate adsorption on the mineral surface may occur mainly due to chemical

bonding without forming any precipitates; in the intermediate concentration region, occurrence of surface precipitation may take place in the interface region; at high concentration, oleate may be precipitated by the Ca and Mg species, both at the mineral surface and in the bulk solution. The preferential partitioning of the oleate in the bulk precipitate as opposed to surface precipitate appears to deleteriously affect the flotation of dolomite and calcite. According to Finkelstein (1989), the principal forms of adsorption on the minerals (except in the most acidic solutions) are chemisorbed oleate and surface calcium oleate.

Finkelstein (1989) summarized the reactions and interactions between oleate and calcite, as reproduced below: (|| represents the surface, $\{CaOl_2\}_n$ represents the surface calcium oleate, and $(CaOl_2)_n$ represents the bulk calcium-oleate precipitate):

- **Precipitation**

$$nCa^{2+} + 2nOl^- \leftrightarrow (CaOl_2)_n \qquad (23.)$$

Ultrasonic treatment was used to distinguish the bulk precipitate oleate from the surface oleate. The oleate that resisted ultrasonic treatment was surface calcium oleate, whereas that which was attached more weakly and could be moved by ultrasonic treatment from the surfaces was bulk precipitate.

- **Chemisorption**

$$||CaCO_3 + Ol^- \leftrightarrow ||CaOl^+ + CO_3^{2-} \qquad (24.)$$

$$2||CaCO_3 + (CaOl_2)_n \leftrightarrow 2||CaOl^+ + (CaOl_2)_{n-1} + Ca^{2+} + 2CO_3^{2-} \qquad (25.)$$

In this case, oleate is chemically bonded with lattice metal atoms of mineral on the surface to form a surface compound. The oleate in any one of its several possible forms, free acid, acid salt, ion, etc., is bound to the surface by valence forces of reactions (Finkelstein, 1989). The presence of chemisorption was supported by the following observations: the formation of a distinct and unique surface entity at low coverage irrespective of the presence of water, the highly irreversible reaction, and a high degree of

selectivity with respect to the mineral for both the adsorption and flotation behavior (Finkelstein, 1989).

- **Physisorption**

$$||CaCO_3 + OI^- \leftrightarrow ||CaCO_3OI^- \quad (26.)$$

$$2||CaCO_3 + (CaOI_2)_n \leftrightarrow 2||CaCO_3OI^- + (CaOI_2)_{n-1} + Ca^{2+} \quad (27.)$$

Several investigators have considered that chemisorption only plays a part in the initial interaction. Hu et al. (1986) concluded that chemisorption is followed by a physisorption.

- **Formation of surface calcium oleate**

$$||CaOI^+ + mCa^{2+} + 2mOI^- \leftrightarrow ||CaOI^+ \cdot \{CaOI_2\}_m \quad (28.)$$

$$||CaOI + (CaOI_2)_n \leftrightarrow ||CaOI^+ \cdot \{CaOI_2\}_m + (CaOI_2)_{n-m} \quad (29.)$$

$$||CaOI^+ \cdot (CaOI_2)_n \leftrightarrow ||CaOI^+ \cdot \{CaOI_2\}_m \cdot (CaOI_2)_{n-m} \quad (30.)$$

Finkelstein (1985) claimed that oleate chemisorbed on the mineral surfaces, and precipitation of calcium oleate took place using the reagent-covered surface as a nucleus. Surface calcium oleate formed on top of the single layer of chemisorbed oleate and could form deposits that were several molecules in thickness. It did not involve the displacement of strongly held, chemisorbed water. The presence of surface calcium oleate is supported by the appearance of the doublet absorption in the infrared spectra, which is caused by the asymmetric stretching of the carbonyl group. Each calcium ion is coordinated with two oleate groups for the infrared spectrum is identical to that of calcium oleate precipitated in bulk.

- **Coagulation**

$$||CaOI^+ + (CaOI_2)_n \leftrightarrow ||CaOI^+ \cdot (CaOI_2)_n \quad (31.)$$

$$||CaOI^+ \cdot \{CaOI_2\}_m + (CaOI_2)_n \leftrightarrow ||CaOI^+ \cdot \{CaOI_2\}_m \cdot (CaOI_2)_n \quad (32.)$$

A number of observations support the proposal that bulk precipitates attach to the regent-covered mineral surfaces by weak forces of coagulation. Giesekke and Harris attributed the depression of calcite by quebracho and wattle tannins to their dispersant action on calcium oleate.

1.6.4 Applications of carbonate flotation

The removal of carbonate minerals such as calcite and dolomite from phosphate ore has been studied extensively (Abdel Khalek, 2001; Matis and Gallios, 1989; Moudgil and Chanchani, 1985). Elgillani and Abouzeid (1993) summarized the theoretical and experimental contribution to the flotation of carbonate from phosphate ores in acidic media. Three calcitic-dolomitic phosphate ores were successfully upgraded by flotation using oleate as a collector. Anazia and Hanna (1987) introduced a selective flotation scheme for carbonate removal from sedimentary apatite, which was achieved under acidic pH without a specific apatite depressant.

1.7 Depression of sulfide mineral flotation

1.7.1 Sulfide flotation

Xanthates are the most common collectors for the flotation of sulfide minerals. When xanthate reacts with the sulfide minerals, two different hydrophobic species are formed on the mineral surfaces: one is an oxidation product of xanthate, dixanthogen, designated as X_2, and the other is a metal xanthate salt, designated as MX. Corresponding to these two products, there are two different reaction mechanisms: electrochemical adsorption and chemisorption.

- **Chemisorption**

The following reactions are proposed (Fuerstenau et al., 1985; Chander, 1996):

(1) Oxidation of sulfide mineral surface

$$MS_{(s)}+2O_2 \rightarrow M^{2+}+SO_4^{2-} \qquad (33.)$$

$$xS^{o} + yH_2O \rightarrow S_xO_y + 2yH^{+} + (2y\text{-}2)e^{-} \quad (34.)$$

(2) Chemisorption of xanthate on the mineral surface

$$M^{2+} + 2X^{-} \rightarrow MX_2 \quad (35.)$$

- **Electrochemical adsorption**

The following reactions are proposed (Chander, 1996; Fuerstenau et al., 1985; Woods, 1984):

(1) Anodic oxidation of xanthate ion on surface of minerals

$$(i)\ X^{-} \leftrightarrow X_{(ads)} + e^{-} \quad (36.)$$

$$(ii)\ 2X_{(ads)} \leftrightarrow X_2 \quad (37.)$$

$$X^{-} + X_{(ads)} \leftrightarrow X_2 + e^{-} \quad (38.)$$

(2) Cathodic reduction of adsorbed oxygen

$$(i)\ O_{2(ads)} + 2H_2O + 2e^{-} \leftrightarrow H_2O_2 + 2OH^{-} \quad (39.)$$

$$(ii)\ H_2O_2 + 2e^{-} \leftrightarrow 2OH^{-} \quad (40.)$$

$$O_2 + 2H_2O + 4e^{-} \leftrightarrow 4OH^{-} \quad (41.)$$

(3) Electron transfer occurs through the solid (such as pyrite, FeS_2):

$$FeS_2 \quad 2e \begin{cases} \rightarrow O_{2(ads)} + 2H_2O + 4e^{-} \leftrightarrow 4OH^{-} & (42.) \\ \leftarrow 2X^{-} \leftrightarrow X_2 + 2e^{-} & (43.) \end{cases}$$

(4) Overall reaction:

$$2X^{-} + 1/2O_{2(ads)} + H_2O \leftrightarrow X_2 + 2OH^{-} \quad (44.)$$

This mechanism takes effect up to about pH 11 because above this pH xanthate ion is the stable form of xanthate. The dixanthogen at the surface of sulfide may form the hydrophobic coatings.

Allison et al. (1972) observed dixanthogen on the surface of pyrite, arsenopyrite, pyrrhotite, molybdenite and chalcopyrite, and metal-xanthate on the surfaces of bornite and galena. Fuerstenau (1985) claimed that cuprous xanthate also existed on chalcopyrite surfaces.

1.7.2 Depression of sulfide flotation

According to the summary of Chander (1985), if X_2 is the hydrophobic entity, depression of the sulfide mineral could be achieved through one or more of the following:

(1) Oxidize the mineral to form a hydrophilic layer such as an oxide or a hydroxide;

(2) Destroy X_2 by a reducing reagent; or

(3) Form a hydrophilic coating of a metal-depressant salt chemically or electro-chemically

If MX is the hydrophobic entity, depression of the sulfide minerals could be achieved through one or more of the following:

(1) Oxidize the mineral to form a hydrophilic coating;

(2) Destroy MX by oxidation or reduction

(3) Destroy MX by hydrolysis or

(4) Form a hydrophilic coating by the depressant chemically or electrochemically.

Therefore, the avenues that can be used to depress sulfide mineral flotation is to hinder collector adsorption onto the mineral surface, to remove the hydrophobic entity from the mineral surface, or to form a hydrophilic layer on the mineral surface.

- **Depression with hydroxyl**

Fuerstenau et al. (1985) attributed the depression function of hydroxyl to the following reasons: first, the formation of hydrophobic dixanthogen was prevented by the relatively high hydroxyl activities. The reaction in equation (44.) will proceeds to the left;

secondly, a hydrophilic film of ferric/ferrous hydroxides would form to hinder the adsorption of xanthate; thirdly, the adsorption of calcium ions on the mineral surface would hinder the adsorption of xanthate on the mineral surface when lime is used as a source of the OH^- ions.

- **Depression with cyanide**

Elgillani and Fuerstenau (1968) conducted a detailed study using cyanide as a depressant for sulfide. They concluded that both CN^- and $Fe(CN)_6^{4-}$ were effective depressants for sulfide. Cyanide formed a hydrophilic film on the mineral surface by forming complexation compounds. The reactions were as follows:

$$Fe^{2+} + 6CN^- \leftrightarrow Fe(CN)_6^{4-} \quad (45.)$$

$$Fe^{2+} + 18CN^- \leftrightarrow Fe_4[Fe(CN)_6]_3 \quad (46.)$$

- **Depression with sulfite or sulfide (SO_3^{2-}, S^{2-}, HS^-)**

Dixanthogen is the hydrophobic species responsible for the flotation of some sulfide minerals. Therefore, reagents that are more reducing than the xanthate-dixanthogen couple could function as depressants (Fuerstenau et al., 1985). Sulfite and sulfide belong to this type of depressant.

$$\text{(i) } SO_4^{2-} + H_2O + 2e^- \leftrightarrow SO_3^{2-} + 2OH^- \qquad E^\circ = -0.93V \quad (47.)$$

$$\text{(ii) } S^\circ + 2e^- \leftrightarrow S^{2-} \qquad E^\circ = -0.48V \quad (48.)$$

$$X_2 + 2e^- \leftrightarrow 2X^- \qquad E^\circ = -0.06V \quad (49.)$$

The couple of sulfide or sulfite is sufficiently reducing to decompose the dixanthogen so as to depress the flotation of sulfide minerals.

In addition, metal sulfides could be more stable than the corresponding metal xanthate, so that chemisorption of xanthate may be retarded (Fuerstenau et al., 1985).

$$MX_2 + S^{2-} \leftrightarrow MS + 2X^- \quad (50.)$$

1.7.3 New methods for the flotation depression of sulfide minerals

The traditionally used depressants as mentioned above have some drawbacks: hydroxide may not have any effect on some minerals such as chalcopyrite because both dixanthogen and chemisorbed xanthate form on the mineral surface and hydroxide can only hinder the formation of dixanthogen. Other depressants are either extremely toxic, or /and strongly reducing so very high dosage is required in an aerated flotation pulp.

The use of organic depressants is an alternative because they offer unique advantages over inorganic depressant for their environmentally friendly characteristics: non-toxic, degradable, and easy to modify (Liu and Zhang, 2000). For example, organic molecules can be designed to suit the requirements such as stability, reducing power, coordinating ability, hydrophilicity and solubility and cost (Nagaraj et al., 1986). The following organic chemicals were used or tested as depressants for sulfide minerals recently.

- **Short-chain organic thiol compounds**

Short-chain organic compounds containing the -SH group, such as thioglycollic acid, were found to be effective depressants for sulfide minerals (Nagaraj, 1986). The complexing group –SH was reported to be the active group and polar groups such as –OH, –COOH, and –P(O)OH impart sufficient hydrophilicity to make them efficient depressants. The reducing power of these reagents increases their depression effects. Thioglycollic acid (TGA) has been successfully used in Cu-Mo separation on a commercial scale. Compared to traditional inorganic reagents such as NaHS, NaCN and P_2S_5, it has the advantage of producing an improved concentrate grade, providing an easily controllable froth at a relatively low dosage. It is also less toxic (Raghavan and Unger, 1983).

Raghavan and Unger (1983) first carried out detailed investigations of the depression mechanism of TGA on chalcocite. They found that thioglycollic acid in solution was progressively and rapidly oxidized to dithiodiglycollic acid (DTGA) by the catalytic action of chalcocite. Their kinetic data showed that an adsorbed TGA molecule reacts with aqueous TGA to form DTGA. The proposed electrochemical reactions are as follows:

$$\text{Anode: } TGA_{(ads)} + TGA_{(aq)} \rightarrow DTGA + 2H^+ + 2e^- \quad E^o_{ox}=0.33V \qquad (51.)$$

$$\text{Cathode: } 1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E^o_{ox}=1.23V \qquad (52.)$$

By examining the flotation behavior of chalcocite in the presence of TGA and DTGA, they concluded that both TGA and DTGA acted as effective depressants in certain pH ranges. DTGA was the least effective at pH 10 and TGA at pH 7. However, they did not mention whether the resulting DTGA remained adsorbed on the surface or went into solution, nor did they explain how the TGA and DTGA molecules adsorbed on the surface (Poling and Liu, 1986). Poling and Liu (1986) therefore studied the adsorption of TGA on the chalcopyrite surface by infrared spectroscopy. They found that either the –SH or –COOH group or both can adsorb on the mineral surfaces, but the –COOH group adsorption appeared to be stable only in the absence of xanthate. Therefore, only the –SH group can be firmly adsorbed on the mineral surface, displace adsorbed xanthate and compete for surface sites with the xanthate. On the basis of their adsorption model, they assumed that the formation of DTGA dimers might enhance the multiplayer adsorption of TGA on the mineral surface.

Chen et al. (2001) studied the effects of thioglycollic acid on the rest potential and zeta potential of sulfide minerals. They found that galena, pyrite and chalcopyrite could be well depressed by TGA, but sphalerite and arsenopyrite could not be depressed. They attributed the depression of sulfide minerals by TGA to an electrochemical mechanism, in which the dixanthogen adsorption on the mineral surface was unstable in the presence of TGA.

- **Polymers**

Polymers, especially natural organic polymers such as starch and dextrin, are non-toxic, biodegradable, cheaper and more resistant to oxidation than inorganic depressants (Liu et al., 2000). Starch and dextrin are reported to be used for copper-lead separation from the bulk concentrates and are also used for depression of carbonaceous pyrite (Bulatovic, 1999).

The hydroxyl groups in starch and dextrin polymer chains are the functional groups in the depression of minerals. Liu and Laskowski (1989, 1989a, 1989b) revealed that the adsorption of starch and dextrin was through the interaction of hydroxyl groups with metal hydroxide species on the mineral surface. They also found that adsorption of the dextrin on galena strongly depended on pH, while adsorption of dextrin on chalcopyrite was much lower and not strongly depended it on pH.

- **Modified polymers**

The depressive behavior of polymers in the differential flotation of sulfide minerals is not as specific as inorganic depressants. The metal ions derived from dissolution of minerals mask the surfaces of minerals and make them all similar (Liu et al., 2000). Substitution of foreign functional groups may be the promising way to increase their selectivity.

Sasaki et al. (1987) used an artificial mixture (1:1 by weight) of galena and chalcopyrite to study the effects of starch xanthate depressant on their separation using potassium ethyl xanthate (KEX) as a collector. The starch xanthate they synthesized was reported to contain a xanthate radical per 82 glucose units. Galena was depressed preferentially by starch xanthate. They compared the result with a soluble starch. From their data, it seems that at low pH, selectivity of the starch xanthate is better than the soluble starch. At high pH, the soluble starch is more selective. They also studied the mechanism of starch xanthate as a depressant in this system, and proposed that KEX was adsorbed on galena forming a multiplayer lead xanthate by metathesis reaction with oxidized products on galena surfaces, thus producing a hydrophilic multiplayer film on galena surfaces. However, the KEX was adsorbed on chalcopyrite surfaces as a monolayer that ensures the hydrophobicity of the chalcopyrite surface. They also explained why the selectivity of starch xanthate was better than that of starch at acidic pH.

Bulton et al. (2001) studied the depression of pyrite by low molecular weight polyacrylamide (PAM) when separating copper activated sphalerite from pyrite with

xanthate. Carboxyl, sulfonate, hydroxyl, or thiourea functional groups were attached to PAM. They found that all the PAM depressed pyrite with little or no effect on sphalerite.

- **Diethylenetriamine (DETA)**

Kerr et al. (1991) and Marticorena et al. (1994) reported that pyrrhotite was depressed by diethylenetriamine (DETA). Kelebek et al. (1998) found that pyrrhotite can be depressed more effectively when DETA was combined with SO_2. Basilio (1992) studied the depression mechanism of DETA on pyrrhotite using LIMS, XPS and FTIR, and concluded that pyrrhotite was activated by heavy metal ions such as Cu^{2+}, Ni^{2+}, Ag^{2+} present in the plant water. The addition of DETA removed the heavy metal ions from the surface of pyrrhotite. The sulfides of heavy metals formed on the pyrrhotite surface were insoluble under reducing conditions. Oxidation of these products made it soluble in the presence of DETA. This explained why DETA was more effective when the ore was oxidized. FTIR spectra of pyrrhotite conditioned with DETA showed no trace of DETA on the surface of pyrrhotite, indicating that DETA acted as a complexing agent instead of being adsorbed on the pyrrhotite surface.

- **Bacteria**

When the ore being treated contains high hydrocarbon, for example, coal pyrite, depression of the pyrite is very difficult. Researchers have studied the depression of pyrite by microorganisms, particularly the bacteria thiobacillus ferrooxidans (Atkins et al., 1987; Elzeky and Attia, 1987; Ohmura et al., 1993).

Elzeky and Attia (1987) showed that bacteria can specifically and selectively attach themselves to pyrite. The flotation of pyrite from both synthetic coal/pyrite mixtures and high sulfur coals could be depressed, while flotation was conducted by conditioning at pH 2 and floating at pH 7-9. Kawatra and Eisele (1999) studied the bacteria depression of both mineral pyrite and coal pyrite. They found that the microorganisms were effective depressants at a high dosage under acid conditions, at which the mineral pyrite was normally floatable and could not be depressed by other depressants. Coal pyrite could be depressed at neutral pH.

2 OBJECTIVE OF THIS RESEARCH

Reverse flotation of carbonate minerals from refractory gold-bearing sulfide ores requires the flotation of the carbonate minerals (calcite, dolomite, siderite, etc.) while depressing sulfide minerals and native gold. The flotation of carbonate using an oxyhydryl collector such as sodium oleate is well established. However, the depressing of sulfide minerals and gold when the oxyhydryl collectors are used as collectors has not been studied, although much information on the depression is available when sulfhydryl collectors are used.

The objective of this research is, therefore, to identify selective depressants for typical sulfide minerals when using sodium oleate to float carbonate from carbonate/sulfide mineral mixtures, and to study the mechanism of action of the depressants. Selective depressants for native gold will not be sought not only because the experiments would otherwise be extremely expensive, but also because any native gold particles floated into the carbonate concentrate could be easily recovered by a direct cyanide leach.

3 EXPERIMENTAL

3.1 Materials

Calcite, dolomite, pyrite and chalcopyrite were all purchased from Ward's Scientific Establishment, Inc. The first three minerals were used without upgrading except that during crushing some of the obvious impure particles were picked out. The chalcopyrite was purified on a Frantz Isodynamic Separator after pulverization. Table 4 shows the chemical analyses of these mineral samples. X-ray diffraction analyses were performed on all minerals, which confirmed their identities and relative purities.

Table 4 Chemical analysis of mineral samples

Sample	Origin	Assay, %							%
		Cu	Fe	S	Ca	Mg	Si	Al	Mineral
Calcite	Creal, Mexico	n/a	0.06	n/a	35.0	0.16	0.11	2.57	87.5
Dolomite	Sussex Co., USA	n/a	0.81	n/a	18.2	12.1	0.18	2.45	92.8
Pyrite	Huanzala, Peru	n/a	44.4	32.3	0.79	0.04	0.07	0.01	95.1
Chalcopyrite	Durango, Mexico	26.8	17.7	25.8	6.41	0.08	4.43	0.65	77.1

n/a: not assayed.

Lumps of the mineral samples were crushed in a laboratory jaw crusher to -20 mm and in a laboratory cone crusher to -2 mm. Impurity particles were picked out after crushing. The crushed sample was then ground in a stainless steel Brinkmann pulverizer, and dry screened into -0.106+0.038 mm and -0.038 mm size fractions. The former was used for flotation tests and the latter for adsorption and electrokinetic potential measurements. The samples were stored in capped plastic bottles. The bottles containing pyrite and chalcopyrite samples were filled with nitrogen, sealed with Parafilm film and stored in a freezer at -4°C.

3.2 Reagents

Sodium oleate (NaOl), with an oleate content >82%, was purchased from Riedel-deHaen and was used without purification. Thioglycollic acid (TGA) was purchased from Sigma-Aldrich with a purity of more than 98%. Ethylene diamine tetraacetic acid (EDTA), citric acid (CA), Na_2CO_3, HCl, NaOH, I_2 and KI are all of analytical grades and were purchased from Fisher Scientific. They were used directly without further purification. Distilled water was used in all experimental work. Stock solutions of sodium oleate, citric acid and thioglycollic acid were prepared everyday at a concentration of 1×10^{-3} mol/L.

3.3 Microflotation

Flotation tests were conducted in a microflotation tube that was described by Francis and Liu (2003). The schematic of this microflotation tube is shown in Figure 8. In a typical flotation test, two grams of –0.106+0.038 mm mineral sample were conditioned in a 250 mL beaker with 100 mL of solution for 2 minutes at the natural pH, followed by 3 minutes of conditioning after the suspension pH was adjusted to the desired value using NaOH or HCl. A depressant was then added and the pulp conditioned for 3 minutes, followed by the addition of NaOl and 3 minutes of conditioning. The conditioned sample was transferred to the microflotation tube and floated for 10 minutes with nitrogen at a flow rate of 10 mL/minute. The stable value of pH before flotation was recorded and reported. For single mineral tests the dry weights of the concentrate and tail were measured and used to calculate recovery directly. For mineral mixtures, the concentrates and tails were assayed for Ca, Mg, Fe or Cu by atomic adsorption spectroscopic analysis according to the method described by Donaldson (1982). These assays were then combined with the weights of the concentrates and tails to calculate the distribution of the minerals after flotation.

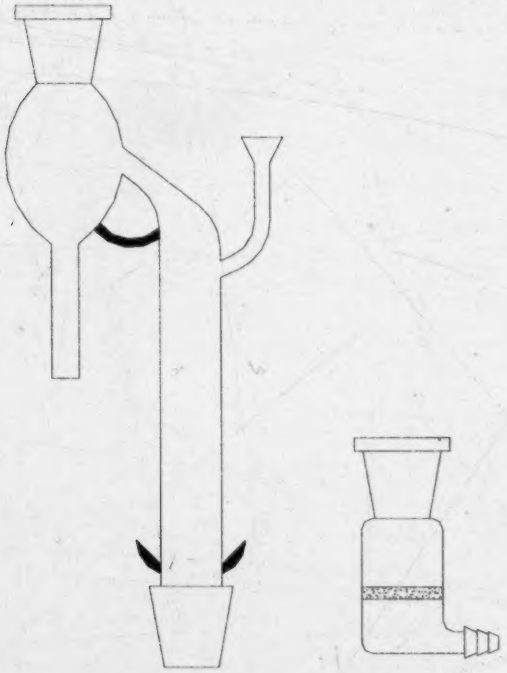


Figure 8 Schematic of microflotation tube

3.4 Electrokinetic potential measurements

- **Procedure**

One gram of –38 μm mineral sample was ground with an alumina mortar and pestle. The ground minerals were placed into a 250 mL beaker with 100 mL 0.01M KNO_3 solution and conditioned for 3 minutes, followed by 5 minutes of conditioning after adding some of the flotation reagents. The suspension was then allowed to settle for 3 minutes. A portion of the supernatant was transferred into a standard cuvette for electrokinetic potential (zeta potential) measurement. Solution temperature was maintained at 25±0.2°C. Ten measurements were taken and the average was reported as the measured value.

- **Principle**

The electrokinetic potential (zeta potential) was obtained with a ZetaPlus zeta potential analyzer. An overview of the ZetaPlus instrument is presented in Figure 9 (Brookhaven Instrument Corporation, 2000). The particles move towards either the positive or the negative pole of the applied field because of their surface charge. The direction in which the particles follow is an indication of the sign of the charge they carry and the velocity at which they move is proportional to the magnitude of the charge. The measured direction and velocity of the particles under the influence of a known electric field can be used to calculate the mobility of particles and their zeta potentials.

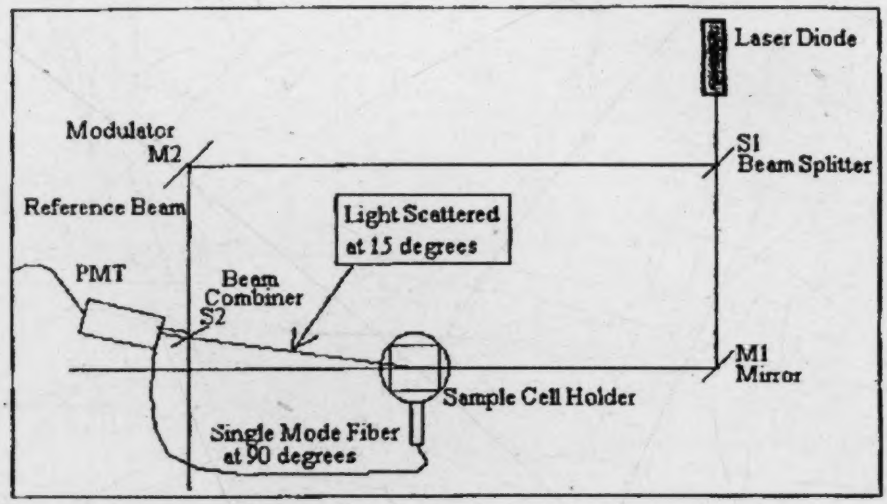


Figure 9 Heterodyne optics used for ZetaPlus instrument

The velocity of particles is measured by the Doppler shift of frequency of light scattered by the particles moving in the applied electric field. The Doppler shift is proportional to the velocity of the particles. Optical heterodyning was used to detect the small shift of the frequency, which is very small compared to that of the laser light being used (Brookhaven Instrument Corporation, 2000).

The mobility (μ_e) was calculated from the velocity of particles (V_s) in the applied electric field (E) according to the following equation (Brookhaven Instrument Corporation, 2000):

$$V_s = \mu_e E \tag{53.}$$

The relationship between zeta potential and mobility depends on the theoretical model selected. There are two classic models, the Smoluchowski and the Huckel models, which apply in two opposite limits.

Huckel limit:

$$\mu_e = (2\varepsilon\zeta)/(3\eta) \qquad \kappa a << 1 \tag{54.}$$

Smoluchowski:

$$\mu_e = \varepsilon\zeta/\eta \qquad \kappa a >> 1 \tag{55.}$$

Where ? is zeta potential, η is the viscosity of the suspending liquid, ε is permitivity of liquid, κ^{-1} is the Debye length, and a is the radius of the particle.

For typical colloids and salt concentrations, the Smoluchowski limit is more appropriate than the Huckel limit. Therefore, the Smoluchowski equation was used to convert mobility to zeta potential (Brookhaven Instrument Corporation, 2000).

3.5 Determination of concentration of TGA

- **Principle:**

The determination of thioglycollic acid was carried out by the quantitative estimation of mercapto groups. Every two mercaptan groups is oxidized to a disulfide by one iodine and the colored iodine itself is reduced to the colorless hydroiodic acid. The reaction can be represented by the following equation:

$$2HSCH_2COOH + I_2 \rightarrow HOOCCH_2SSCH_2COOH + 2HI \tag{56.}$$

- **Procedure:**

The method used was similar to that described by Walker (1953) with a slight modification. The procedure is as follows: a given amount of TGA solution was transferred quantitatively to a 250 mL conical flask, and 50 mL distilled CO_2 free water was then added, together with 1 mL of 2N H_2SO_4 solution. The flask was then stoppered and stirred on the magnet stirrer to ensure that the thiol compound was dissolved. The stopper was then removed and the contents of the flask were titrated immediately with standard iodine solution to a yellow endpoint. The standard solution was prepared as follows: 12.7 grams iodine and 40 grams potassium iodide are placed into a 250 mL beaker and made into a paste by adding 25 mL distilled water. The paste was stirred until all the iodine was dissolved, and then diluted to 1 L with distilled water. Before titration, the stock solution was diluted 10 times.

3.6 FTIR spectroscopic measurement

- **Sample Preparation**

Pyrite and chalcopyrite treated with reagents:

Two grams of –38 μm pure pyrite or chalcopyrite was ground to about –2 μm in an alumina mortar, and then placed into a 250 mL beaker with 100 mL of 1×10^{-1} mol/L reagent. After the pH of the suspension was adjusted to the desired value using NaOH, the suspension was conditioned for 20 minutes. The conditioned pyrite or chalcopyrite was separated from the solution using a centrifuge. The sample was washed four times with distilled water and then dried under vacuum at room temperature for 24 hours.

TGA - copper salt (with TGA overdosage):

100 mL of 1×10^{-1} mol/L TGA was placed into a 250 mL beaker, and then 50 mL of 1×10^{-2} mol/L $CuSO_4\cdot5H_2O$ was added. A black precipitate was formed. After 0.5 minutes of agitation, the precipitate was separated from the liquid using a centrifuge. The

precipitate was washed four times using distilled water and dried in vacuum at room temperature. The resulting sample was then ground for FTIR analysis.

TGA – copper salt (with copper sulfate overdosage):

100 mL of 1×10^{-2} mol/L $CuSO_4 \cdot 5H_2O$ was placed into a 250 mL beaker, and then 50 mL of 1×10^{-1} mol/L TGA was added. After 0.5 minutes of agitation, the precipitate was separated from the liquid using a centrifuge. The precipitate was washed four times using distilled water and dried in vacuum at room temperature. The resulting sample was then ground for FTIR analysis.

- **FTIR measurement**

1 - 2 mg of the above solid samples was weighed out, and mixed with 50 mg of KBr in an alumina mortar. The diffuse reflectance spectra of the mixtures were obtained with a FTS 6000 Fourier Transform Infrared Spectrometer. Typical spectra were recorded from an average of 128 scans measured at 4 cm^{-1} resolution with a narrow band liquid nitrogen cooled DTGS/MCT detector. The sample compartment was purged with high purity nitrogen to remove CO_2 and H_2O before the measurement. The main component of this FTIR spectrometer, the Michelson Interferometer, is illustrated in Figure 10.

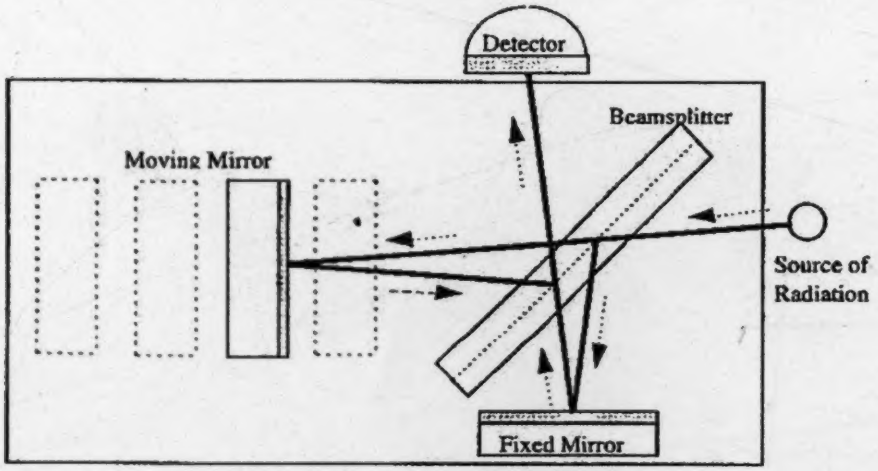


Figure 10 Schematic of the Michelson Interferometer

- **Principle of infrared identification**

Functional groups of molecules absorb infrared light in the same wavenumber range regardless of the structure of the rest of the molecule if the following necessary condition is satisfied (Smith, 1998):

(1) The change in dipole moment of the molecule with respect to distance is nonzero,

(2) The energy of the infrared light impinging on the molecule is equal to a vibration energy level difference within the molecule

There is a correlation between the wavenumber at which a functional group of molecule absorbs infrared radiation and its structure (Smith, 1998):

$$W = (k / \mu)^{1/2} /(2\pi) \qquad (57.)$$

W is wavenumber in cm^{-1}, k is force constant of the functional group in Newton/cm, and μ is the reduced mass of the molecule.

The equation shows that two properties of chemical bonds, force constant and reduced mass, determine the wavenumber at which a molecule absorbs infrared light. A molecule with a strong chemical bond (a large force constant) will adsorb infrared light of a high wavenumber, and a molecule with heavy atoms (a large reduced mass) will absorb at a low wavenumber. This correlation allows the structure of an unknown molecule to be identified from its infrared spectrum, and allows the amount of species present to be determined by the intensity of absorption.

4 FLOTATION TESTS OF SINGLE MINERALS

4.1 Floatability of single minerals with sodium oleate

NaOl is the most widely used collector for carbonate minerals such as calcite and dolomite. A considerable amount of information is available, as summarized by Laskowski (1999), Miller and Keller (1999), Finkelstein (1989) and Somasundaran et al. (1991). However, information on the floatability of pyrite and chalcopyrite with NaOl is scarce.

Figure 11 shows the influence of NaOl concentration on the flotation recovery of calcite, dolomite, pyrite, and chalcopyrite single minerals at pH 10. As can be seen, chalcopyrite floated readily with NaOl, followed by calcite, dolomite and pyrite. With 1×10^{-4} mol/L NaOl, over 90% of the chalcopyrite and calcite and about 80% of the dolomite were floated, but pyrite recovery was only below 20%. When the concentration of NaOl was increased to 2×10^{-4} mol/L, pyrite recovery increased to over 80%.

Figure 12 shows the effect of pH on the recovery of the single minerals at a NaOl concentration of 3×10^{-4} mol/L. All four minerals showed good flotation across the pH range tested (up to 13). This is of particular significance to the separation, since it is different from the common observation that sulfide minerals would be depressed at high pH when xanthate was used as a collector: pyrite was depressed above pH 11 and chalcopyrite was depressed above pH 12 (Fuerstenau, 1982; Fuerstenau et al., 1985).

A species distribution diagram for an aqueous NaOl solution (Pugh and Steniu, 1985) indicated that above pH 10, $RCOO^-$ and $(RCOO)_2^{2-}$ were the dominant species. Our electrokinetic measurements (as will be discussed in Chapter 6) indicated that the surfaces of pyrite were positively charged and chalcopyrite was negatively charged in alkaline solutions. Therefore, the adsorption of the sodium oleate on the surface of pyrite

was probably through coulombic attraction and on the chalcopyrite surfaces was probably through chemical reactions that could overcome the electrostatic repulsion.

The reaction affinity between collector and minerals can be evaluated by the solubility products of collector and the lattice metals of minerals (Du Rietz, 1975). Solubility products of metal hydroxides and metal oleate are listed in Table 5.

Table 5 Solubility products of metal hydroxides and metal oleate

	Ca^{2+}	Mg^{2+}	Cu^{2+}	Fe^{2+}	Fe^{3+}
Oleate ($pK_{sp, M(Ol)n}$)	15.4	13.8	19.4	15.4	34.2
Hydroxide ($pK_{sp, M(OH)n}$)	4.9	10.3	18.2	14.8	37
$p\frac{K_{sp,M(Ol)_n}}{K_{sp,M(OH)_n}}$	10.5	3.5	1.2	0.6	-2.8

*Source: C. Du Rietz (1975)

It can be seen from the solubility products above that there will not be any selectivity when using sodium oleate to float the sulfide and carbonate minerals since the solubility products of metal-oleate of sulfide are larger than those of the carbonate, that is, the oleate group may readily precipitate and adsorb on the sulfide mineral surface.

Since the ratio $p\frac{K_{sp,M(Ol)_n}}{K_{sp,M(OH)_n}}$ reflects the relative stability of the metal-oleate and metal-hydroxyl compounds, it can be used to judge the ease with which metal-oleate is formed and thus the floatability of the mineral with oleate at alkaline pH. From Table 5 we can see that calcite should have an excellent floatability due to its high $p\frac{K_{sp,M(Ol)_n}}{K_{sp,M(OH)_n}}$ ratio. Dolomite, chalcopyrite and pyrite should also be floatable but to a lesser degree. This may explain why pyrite has a low recovery at a low concentration of sodium oleate as shown in Figure 11. It is also seen that $Fe(OH)_3$ is more stable in an alkaline solution and the metal oleate is stable only in the acid and neutral solutions (Jiang et al., 2000), and thus sodium oleate cannot replace hydroxide and adsorb directly

on the surfaces of (oxidized) pyrite. This may explain why pyrite could not be floated when it was oxidized (results is not presented here).

Therefore, both the experimental results and solubility product analysis indicated that sulfide would float together with carbonate when sodium oleate was used as a collector. Selective reverse carbonate flotation using sodium oleate would require a selective depressant for the sulfide minerals.

4.2 Depressants for the sulfide minerals

The traditional reagents used to depress the sulfhydryl collector flotation of sulfide minerals, such as sodium sulfide, sodium cyanide, and sulfur dioxide, etc., are usually reducing agents and environmentally un-friendly, and are deemed inappropriate (Bulatovic and Wyslouzil, 1995; Liu and Zhang, 2000; Nagaraj et al., 1986). Organic depressants, such as starch xanthate, thioglycollic acid, citric acid, and combinations thereof were chosen in this study. Starch xanthate has been tested as a selective sulfide flotation depressant (Nagaraj et al., 1986; Sasaki et al., 1987) and its depressive function can be easily envisaged due to the adsorption functionality introduced by xanthate groups and the large number of –OH groups in the starch. Large number of –OH groups exist in starch xanthate because the degree of substitution by xanthate is usually much lower than three. TGA was shown to be a general depressant for sulfide minerals using xanthates as collectors (Agar, 1984; Poling and Liu, 1986; Raghavan and Unger, 1983). Citric acid is a common chelating agent and has been used by Liu and Zhang (2000) to eliminate the detrimental effect of Ca^{2+} in the flotation separation of chalcopyrite from galena using dextrin. It may be useful in the current carbonate/sulfide flotation system as well.

Based on reagent availability and cost considerations, we did not pursue the use of starch xanthate as a depressant, although a starch xanthate was synthesized and tested in the sodium oleate flotation of pyrite and showed promise.

4.2.1 Thioglycollic acid (TGA)

As shown in Figure 13, TGA did not affect the NaOl flotation of calcite in the concentration range tested (up to 6×10^{-4} mol/L). It only slightly affected dolomite flotation up to a TGA concentration of 5×10^{-4} mol/L, and the effect became significant above this concentration.

TGA showed some depressive effect on chalcopyrite and caused about 20% drop in its recovery at a TGA concentration of 1×10^{-4} mol/L. Further increase in TGA concentration (up to 6×10^{-4} mol/L) did not cause further drop in chalcopyrite recovery.

The depressive effect of TGA on pyrite was interesting in that the strongest depression was observed only at concentrations lower than 1×10^{-4} mol/L. When the concentration was increased, pyrite flotation was gradually restored and reached about 80% at 6×10^{-4} mol/L TGA.

Figure 14 shows the effect of pH on the depressive action of TGA. Again, the flotation of calcite and dolomite was not significantly affected by the presence of TGA. Pyrite was strongly depressed between pH 9 and 10.5 and chalcopyrite was only slightly depressed in this pH range.

4.2.2 Citric acid

Figure 15 and Figure 16 show the depressive effect of citric acid as a function of its concentration and suspension pH. Generally, the shapes of the curves are similar to those of Figures 13 and 14. Citric acid did not have significant depressive effects on the NaOl flotation of calcite and chalcopyrite, but its depressive effect on pyrite and dolomite was stronger than that of TGA, especially at higher concentrations of citric acid. Depression of pyrite by citric acid again appeared between pH 9 and 11 (Figure 16).

The acidity of citric acid is lower than that of TGA, and this may explain why an increasing concentration of citric acid caused a smaller increase in the recovery of pyrite.

4.2.3 Combination of TGA and citric acid

It is known that the ability of citric acid to chelate metals that act as prooxidants enables it to be used as a synergic antioxidant (Bell, 1977). The depressive effect of TGA may be compromised due to its oxidation (to DTGA) which was catalyzed by sulfide minerals in the flotation pulp (Raghavan and Unger, 1983). Therefore, TGA was mixed with citric acid in a 1:1 molar ratio to test if there was any synergistic effect in the depression of sulfide. The depressant thus obtained was called "mixed depressant". The results are presented in Figure 17 and Figure 18.

These two figures clearly show that the mixed depressant was far better than either one used alone. The depression on pyrite was stronger and the lowest recovery was obtained at much lower reagent dosages, although the restoration of pyrite recovery at higher dosages was still observed (Figure 17).

More significantly, chalcopyrite, which was not depressed by either TGA or citric acid alone, was depressed using the mixed depressant in the concentration range of 2×10^{-4} and 4×10^{-4} mol/L. The mixed depressant had no effect on the flotation of calcite, but it depressed dolomite flotation when its concentration was above 2×10^{-4} mol/L.

Figure 18 shows that the mixed depressant had little effect on the flotation of calcite and dolomite (at 1×10^{-4} mol/L). However, the mixed depressant caused strong depression of both pyrite and chalcopyrite between pH 9 and 10.5.

A window of separation between calcite/dolomite and pyrite/chalcopyrite can be seen from Figure 17 and Figure 18, i.e., pH 9 to 11, NaOl 3×10^{-4} mol/L, mixed depressant 1×10^{-4} mol/L (for pyrite) or 2×10^{-4} mol/L (for chalcopyrite).

4.3 Summary

- Calcite, dolomite, chalcopyrite and pyrite could be floated with sodium oleate as a collector. The floatability followed the order calcite > dolomite > chalcopyrite > pyrite. The solubility of metal oleate and metal hydroxide may play a role in the flotation of these minerals by sodium oleate.

- The addition of thioglycollic acid (TGA) and citric acid (CA) did not affect the flotation of calcite and dolomite. When used alone, TGA and CA depressed pyrite at pH 9-11 but did not depress chalcopyrite. A mixture of TGA and CA was a much stronger depressant than either used alone. It not only caused stronger depression of pyrite but also depressed chalcopyrite. However, the mixture of TGA and CA had no effect on the flotation of calcite and slightly depressed the flotation of dolomite.

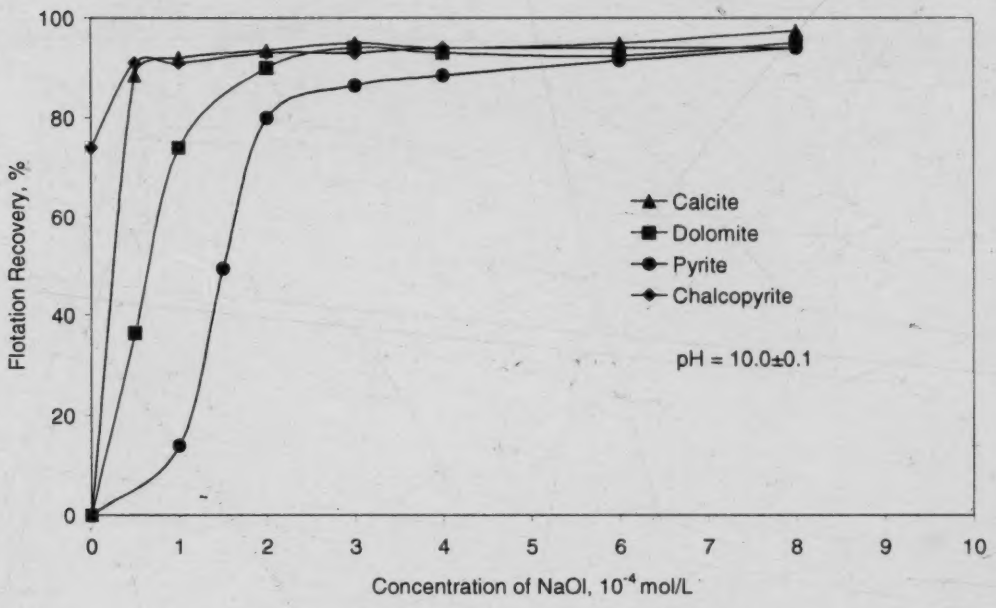


Figure 11 Effect of NaOl concentration on the flotation recovery of single minerals at pH 10.

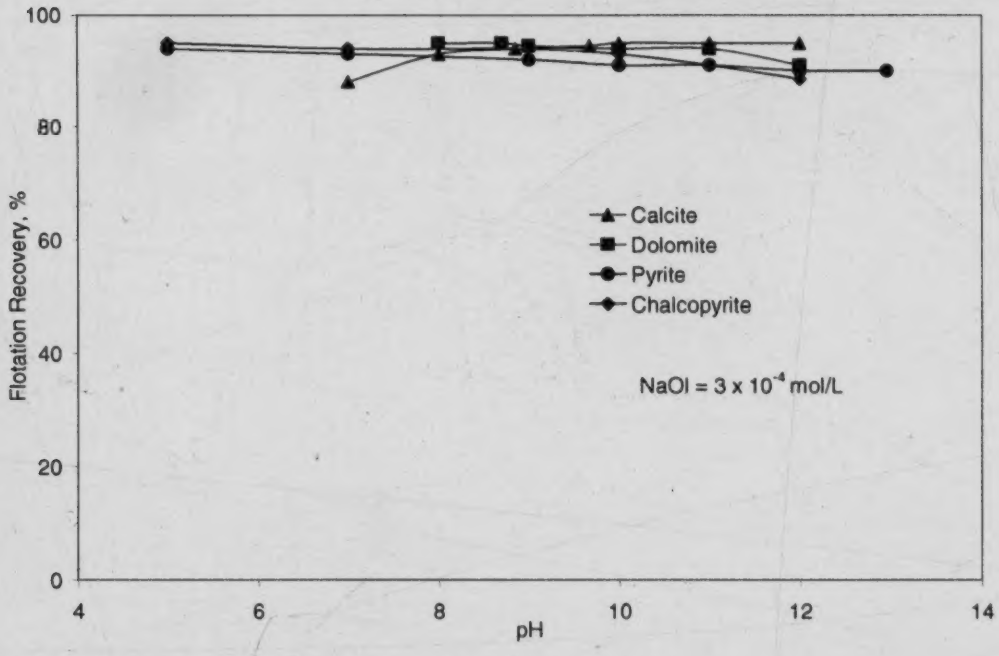


Figure 12 Effect of pH on the flotation recovery of single minerals at NaOl concentration of 3×10^{-4} mol/L.

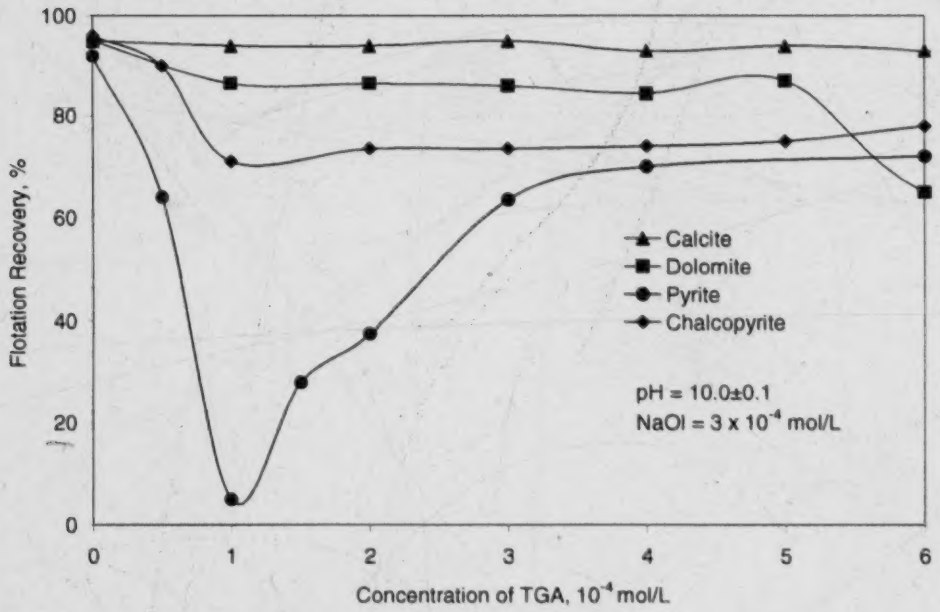


Figure 13 Effect of TGA concentration on the flotation recovery of single minerals at pH 10 and 3×10^{-4} mol/L NaOl.

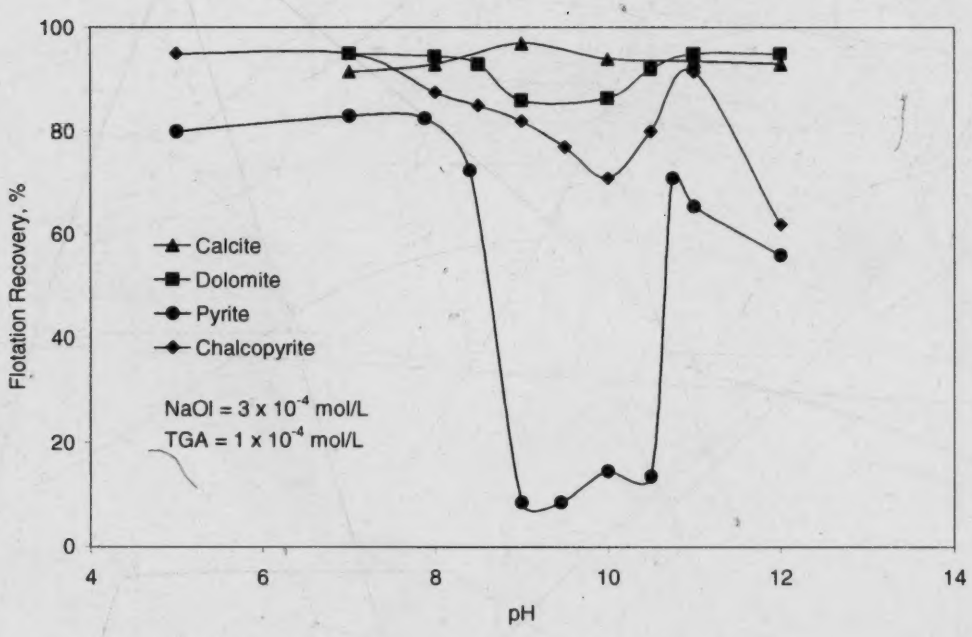


Figure 14 Effect of pH on the flotation recovery of single minerals at 3×10^{-4} mol/L NaOl and 1×10^{-4} mol/L TGA.

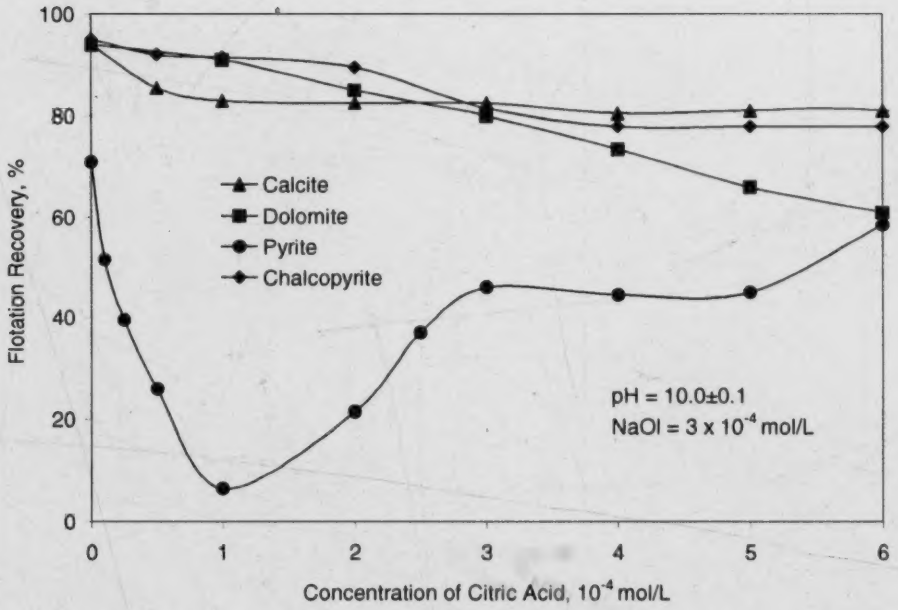


Figure 15 Effect of the concentration of citric acid on the flotation recovery of single minerals at pH 10 and 3×10^{-4} mol/L NaOl.

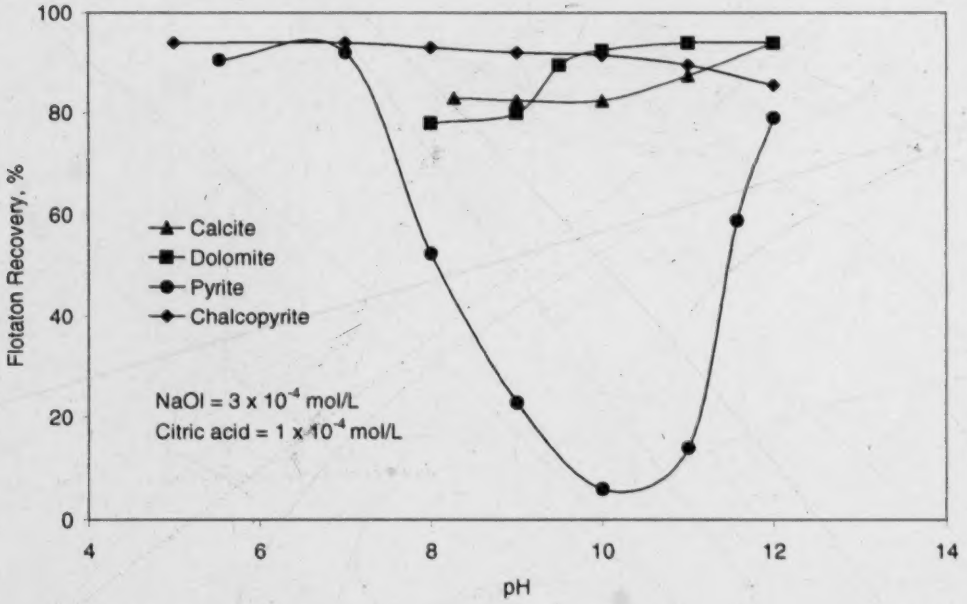


Figure 16 Effect of pH on the flotation recovery of single minerals at 3×10^{-4} mol/L NaOl and 1×10^{-4} mol/L citric acid.

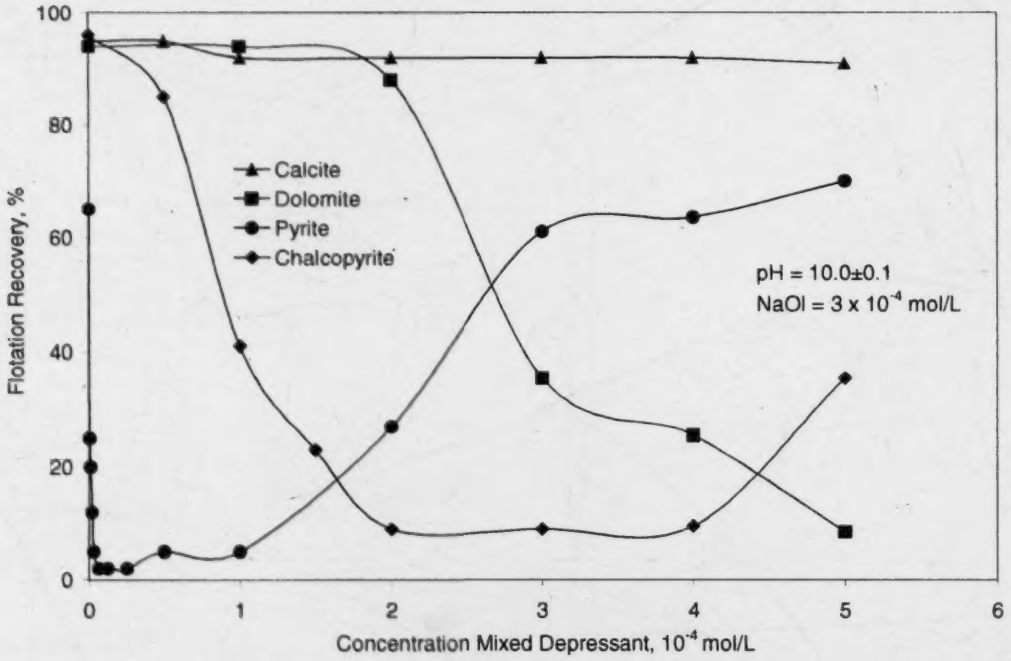


Figure 17 Effect of concentration of mixed depressant on the flotation recovery of single minerals at pH 10 and 3×10^{-4} mol/L NaOl.

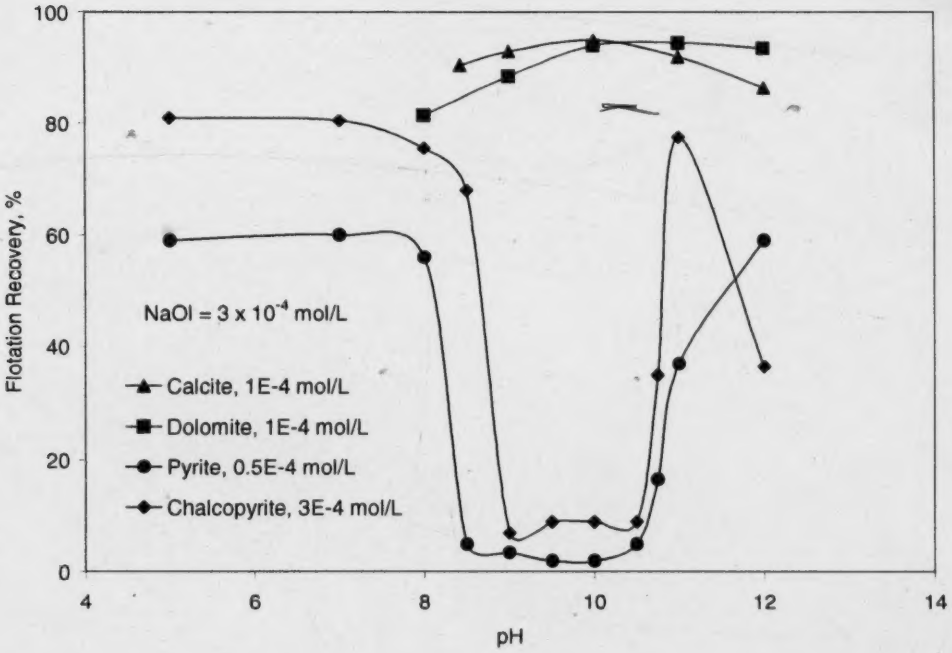


Figure 18 Effect of pH on the flotation recovery of single minerals at 3×10^{-4} mol/L NaOl. Concentration of mixed depressant varied as indicated.

5 TESTS OF MIXTURE OF SINGLE MINERALS

In this series of tests, a carbonate mineral was blended with a sulfide mineral at 1:1 weight ratio and floated using similar procedures established in single mineral flotation tests. At the end of the flotation, the grades of the concentrates and tails were determined by measuring the Ca, Mg, Fe or Cu contents using atomic absorption spectroscopic analysis. A separation efficiency, E, calculated using the following equation, was used to evaluate the separation process (Stevens and Collins, 1961):

$$E = \varepsilon \frac{\beta - \alpha}{\beta_{max} - \alpha} \tag{58.}$$

Here e is the percentage recovery of a carbonate mineral into the flotation concentrate, β and β_{max} are the actual and maximum grade of carbonate mineral in the concentrate, a is the grade of carbonate mineral in the flotation feed. Since the minerals were of high purity and a 1:1 (weight) mineral mixture was used, a was taken as 50%.

5.1 Separation of calcite from pyrite

Figure 19 and Figure 20 show the effect of concentration of the mixed depressant (TGA and CA) and pH on the separation of calcite from pyrite. At around a depressant concentration of 2.5×10^{-4} mol/L, the two minerals were almost perfectly separated and the separation efficiency was maximum. The optimum dosage of the depressant was 2.5 times higher than in the single mineral tests, indicating that interactions between the two minerals had probably occurred.

Figure 20 shows that at a mixed depressant concentration of 1×10^{-4} mol/L, calcite and pyrite could be separated with maximum separation efficiency between pH 9.5 and 11. Below or above this pH range, the separation efficiency was lower because of lower grades of calcite in the concentrate.

5.2 Separation of dolomite from pyrite

Figure 21 shows that the optimum mixed depressant concentration was between 2×10^{-4} mol/L and 2.5×10^{-4} mol/L for dolomite/pyrite separation. Generally, dolomite appeared to be more sensitive to the combined use of TGA and citric acid than calcite and did not float as strongly as the latter. At higher concentrations of the mixed depressant, dolomite was completely depressed, which was consistent with the single mineral tests.

Figure 22 shows that dolomite was more sensitive to pH after it was blended with pyrite. In the single mineral flotation tests, dolomite was unaffected between pH 9 to 11 where both pyrite and chalcopyrite were depressed (Figure 18), so it appeared that there was a window of separation between pH 9 and 11. However, Figure 22 shows that separation efficiency only displayed a narrow and low maximum at around pH 10.

5.3 Separation of calcite from chalcopyrite

Figure 23 shows that calcite could be separated from calcite/chalcopyrite mixtures, and the separation behavior was similar to that of calcite/pyrite. However, the optimum mixed depressant concentration shifted to higher values of about 5×10^{-4} mol/L.

Figure 24 shows that the optimum separation pH range for calcite and chalcopyrite mixtures was narrowed to pH 9.5 - 10.5, and the separation efficiency was lower than that for the calcite/chalcopyrite system. This is in agreement with the results of the single mineral tests (Figure 18).

5.4 Separation of dolomite from chalcopyrite

The separation of dolomite from chalcopyrite was unsuccessful. As Figure 25 shows, dolomite and chalcopyrite were either floated together or depressed together.

In fact, the single mineral flotation tests hinted these results. As Figure 17 shows, when the concentration of mixed depressant was low, chalcopyrite was not depressed; at higher depressant concentrations, both chalcopyrite and dolomite were depressed.

5.5 Summary

The following conclusions can be drawn from the flotation tests on artificial mineral mixtures:

- Calcite could be separated from pyrite using 3×10^{-4} mol/L sodium oleate as a collector for calcite and 2.5×10^{-4} mol/L mixed depressant (TGA and CA) for pyrite at pH 9-11.
- Dolomite could also be separated from pyrite, and the optimum pH range was narrower and separation efficiency was lower.
- Calcite could be separated from chalcopyrite but it required the presence of higher concentrations of the mixed depressants. The optimum pH range was also narrower.
- Flotation separation of dolomite from chalcopyrite was unsuccessful using the reagent schemes developed.

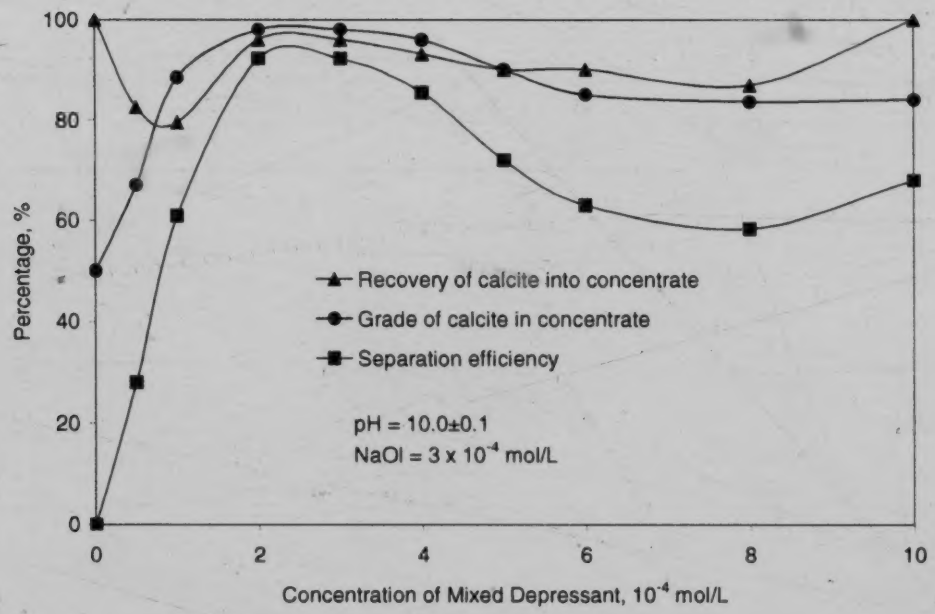


Figure 19 Effect of concentration of mixed depressant on the recovery and grade of calcite in flotation concentrate and the separation efficiency at pH 10 and 3×10^{-4} mol/L NaOl. Flotation feed was a 1:1 (weight) mixture of calcite:pyrite.

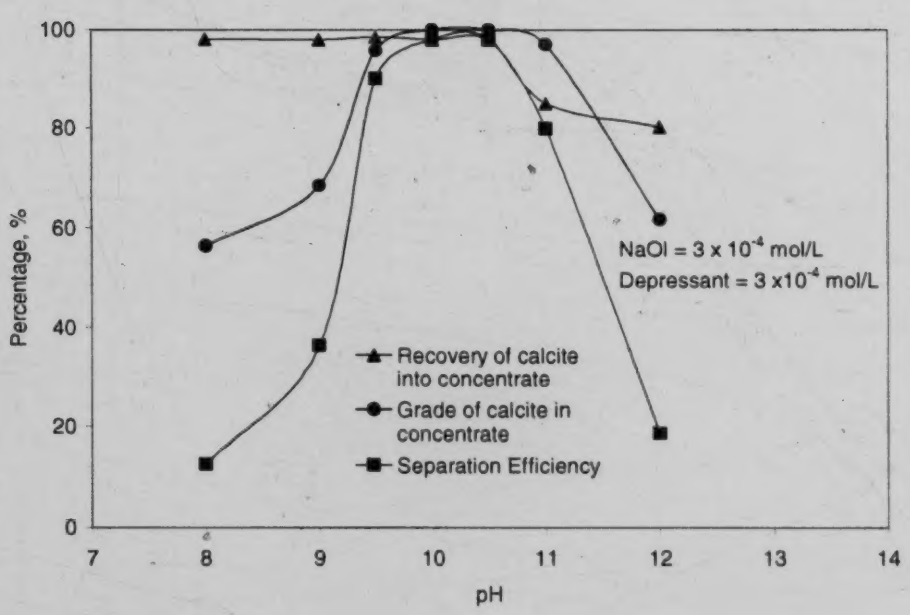


Figure 20 Effect of pH on the recovery and grade of calcite in flotation concentrate and separation efficiency at 3×10^{-4} mol/L NaOl and 3×10^{-4} mol/L mixed depressant. Flotation feed was a 1:1 (weight) mixture of calcite:pyrite.

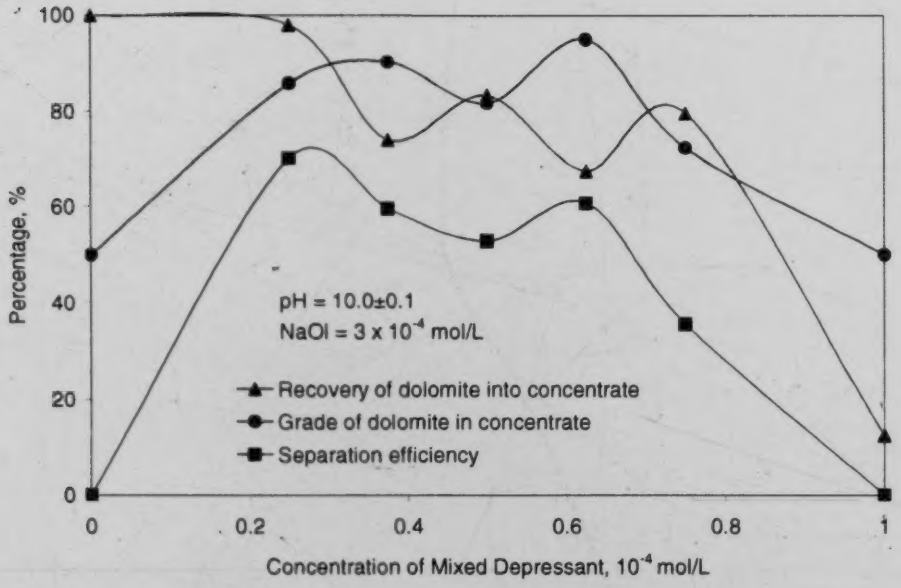


Figure 21 Effect of concentration of mixed depressant on the recovery and grade of dolomite in flotation concentrate and separation efficiency at pH 10 and 3×10^{-4} mol/L NaOl. Flotation feed was a 1:1 (weight) mixture of dolomite:pyrite.

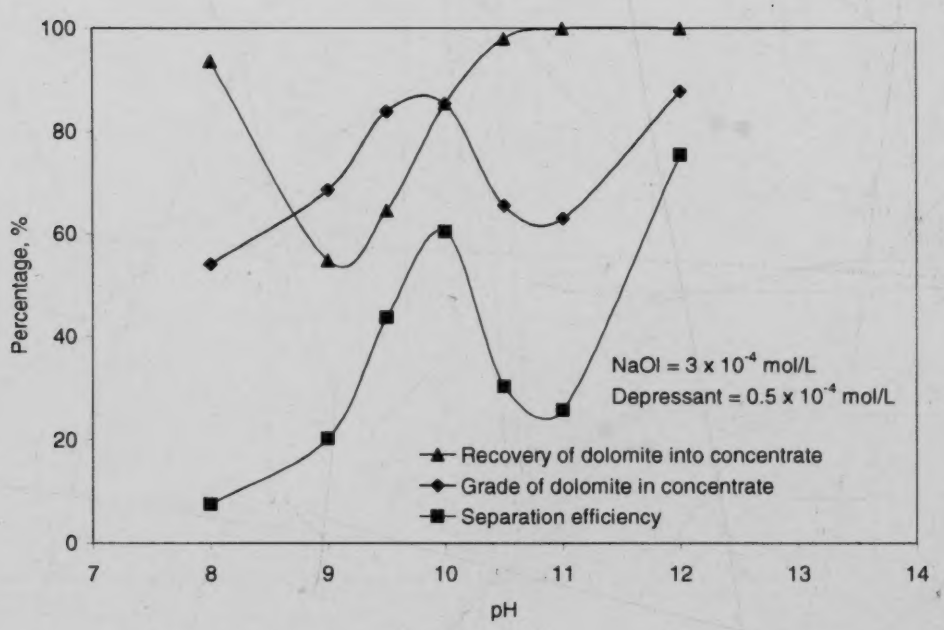


Figure 22 Effect of pH on the recovery and grade of dolomite in flotation concentrate and separation efficiency at 3×10^{-4} mol/L NaOl and 0.5×10^{-4} mol/L mixed depressant. Flotation feed was a 1:1 (weight) mixture of dolomite:pyrite.

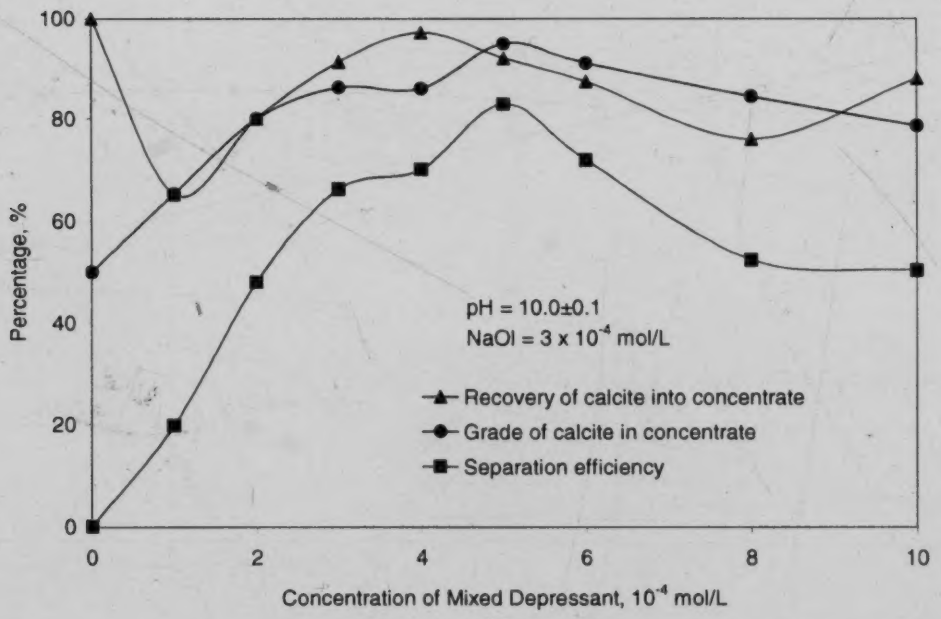


Figure 23 Effect of concentration of mixed depressant on the recovery and grade of calcite in flotation concentrate and separation efficiency at pH 10 and 3×10^{-4} mol/L NaOl. Flotation feed was a 1:1 (weight) mixture of calcite:chalcopyrite.

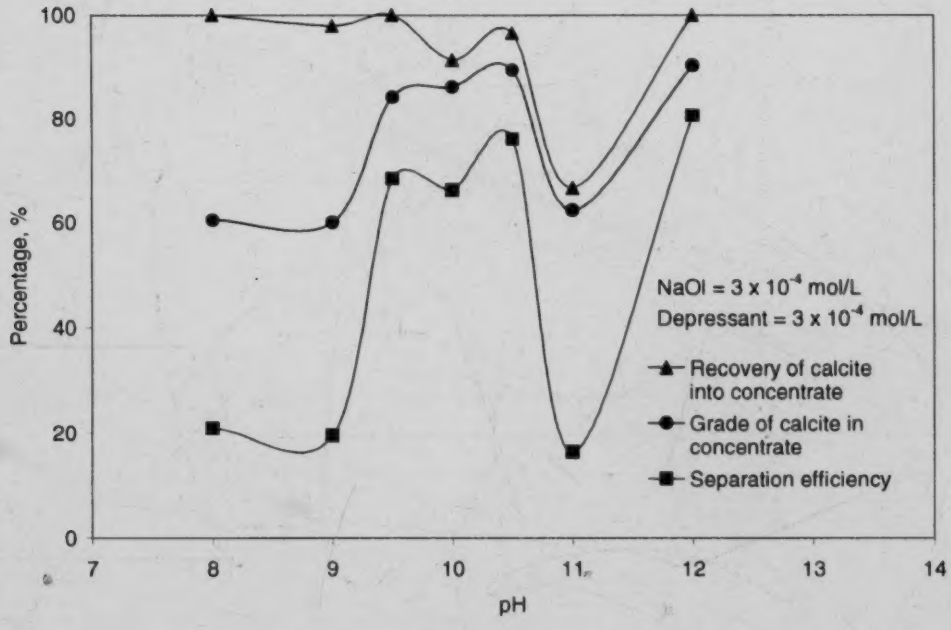


Figure 24 Effect of pH on the recovery and grade of calcite in flotation concentrate and separation efficiency at 3×10^{-4} mol/L NaOl and 3×10^{-4} mol/L mixed depressant. Flotation feed was a 1:1 (weight) mixture of calcite:chalcopyrite.

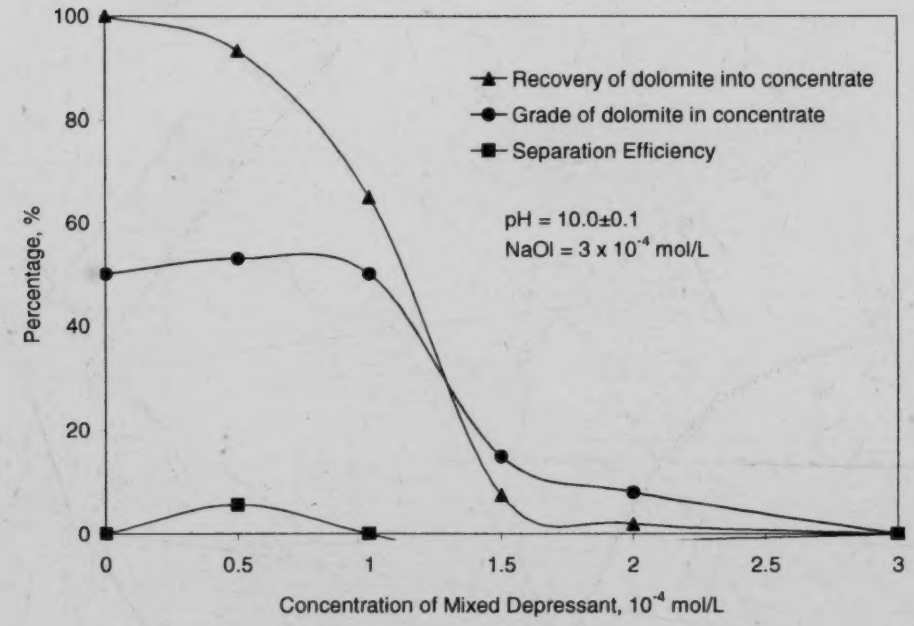


Figure 25 Effect of concentration of mixed depressant on the recovery and grade of dolomite in flotation concentrate and separation efficiency at pH 10 and 3×10^{-4} mol/L NaOl. Flotation feed was a 1:1 (weight) mixture of dolomite:chalcopyrite.

6 MECHANISM OF THE FLOTATION SEPARATION OF CARBONATE FROM SULFIDE MINERALS

It has been shown in the previous two chapters that carbonate minerals, especially calcite, could be removed from sulfide minerals by froth flotation. The flotation procedure could be tested to remove carbonate minerals from refractory gold-bearing sulfide ores. However, since this project was part of a comprehensive program, it was felt that before embarking on real ore testing, it was necessary to understand how the reagent scheme and the flotation procedures made the separation possible. The subsequent research was therefore directed to the study on the mechanism by which the reagent schemes functioned. The techniques employed included solution chemistry, electrokinetic potential measurement, and infrared spectroscopic studies.

6.1 The stability of TGA

One of the most interesting observations in the flotation tests was that TGA did not depress the oleate flotation of chalcopyrite but the combined use of TGA and CA (i.e., the mixed depressant) depressed the chalcopyrite. Based on available literature information, it was suggested that this phenomenon might have been the result of the stability of TGA.

6.1.1 The oxidation of TGA under different conditions

TGA, which is a monocarboxylic acid containing a sulphydryl (–SH) group, is stable at room temperature in less than 70 wt% aqueous solutions. In more concentrated solutions, self-esterification takes place to some extent. It was reported that it could be easily oxidized to dithiodiglycollic acid at high concentration of oxygen (Poling & Liu, 1986). Raghavan (1983) proposed that the surface of chalcocite (CuS_2) acted as a catalyst for the oxidation of TGA to DTGA in air. In order to examine the possible catalysis effects and the role of CA in the mixed depressant (i.e., CA and TGA), the oxidation of

TGA with different reagents under different conditions was studied. The amount of TGA in solution was determined by titration using standard iodine solution.

Figure 26 presents the oxidation of TGA at different pH values when an aqueous solution of TGA was agitated for 2 minutes open to air. It is noted that the oxidation of TGA did not take place in the whole pH range. An alkaline pH favored TGA oxidation. The addition of copper sulfate into the TGA solution only caused a small loss of TGA. The addition of H_2O_2 alone caused about 10 percent loss of TGA below pH 6, and more than 10% above pH 6. When both the copper sulfate and H_2O_2 were added into the TGA solution, the amount of TGA in the solution decreased significantly, especially in the alkaline pH range where only about 10% of the TGA was left.

The oxidation of TGA with exposure time to air was also examined. From Figure 27, it can be seen that at pH 2 TGA was stable within the time period tested (up to 10 minutes). When $CuSO_4$ was added alone, the loss of TGA was negligible. The addition of H_2O_2 caused about 7% loss of TGA. When Cu and H_2O_2 were added together, the amount of TGA in the solution decreased sharply within the first minute, then continuously decreased with exposure time.

From Figure 26 and Figure 27, it can be seen that copper ions had a catalytic effect on the oxidation of TGA in the presence of H_2O_2. This catalytic effect was accelerated at higher pH. This may explain why chalcopyrite could not be depressed by TGA alone.

6.1.2 The role of copper ions and pH in TGA oxidation

TGA goes through two rapid and reversible acid dissociation equilibria in water as follows (Sun & Stanbury, 2002):

$$HSCH_2COOH \leftrightarrow HSCH_2COO^- + H^+ \quad (59.)$$

$$HSCH_2COO^- \leftrightarrow {}^-SCH_2COO^- + H^+ \quad (60.)$$

It is believed that tautomerization between $HSCH_2COO^-$ and $^-SCH_2COOH$ takes place (Sun & Stanbury, 2002):

$$HSCH_2COO^- \leftrightarrow {}^{\cdot}SCH_2COOH \quad (61.)$$

In the presence of an oxidant such as H_2O_2 in TGA solution, the following reactions may take place:

$$HSCH_2COOH + H_2O_2 + H^+ \leftrightarrow [{}^{\cdot}SCH_2COOH]^+ + 2H_2O \quad (62.)$$

$$[{}^{\cdot}SCH_2COOH]^+ + HSCH_2COOH \rightarrow HOOCH_2SSCH_2COOH + H^+ \quad (63.)$$

Here $HOOCH_2SSCH_2COOH$ is dithiodiglycollic acid (DTGA). Reaction 63 is fast and reaction 62 is slow.

It is well known that transition metal ions such as Cu^{2+} and Fe^{3+} can react with TGA and act as a catalyst for the TGA oxidation (Baldea, 1989; Keith et al., 1975). For example, in the presence of copper ions, the following reactions are possible:

$$Cu^{2+} + HSCH_2COOH \leftrightarrow [Cu(SCH_2COOH)]^+ + H^+ \quad (64.)$$

$$[Cu(SCH_2COOH)]^+ + HSCH_2COOH \leftrightarrow Cu(SCH_2COO)_2 + H^+ \quad (65.)$$

$$Cu^+ + HSCH_2COOH \leftrightarrow Cu(SCH_2COOH) + H^+ \quad (66.)$$

$$Cu(SCH_2COOH) + HSCH_2COOH \leftrightarrow [Cu(SCH_2COOH)_2]^- + H^+ \quad (67.)$$

$$[Cu(SCH_2COOH)]^+ + [Cu(SCH_2COO)_2]^- \rightarrow HOOCH_2SSCH_2COOH + 2Cu^+ + {}^{\cdot}SCH_2COOH \quad (68.)$$

$$2Cu^+ + H_2O_2 + 2H^+ \rightarrow 2Cu^{2+} + 2H_2O \quad (69.)$$

Reaction 68 and 69 are the fast steps. It is reported that the catalytic effect is present when the concentration of Cu^{2+} in the solution is more than 6×10^{-7} M (Henry et al., 1979).

The rate of oxidation of TGA in the presence of Cu^{2+} appears to be strongly pH dependent. A rapid increase in oxidation rate is observed when the pH of the solution is increased. One explanation is that the dissociation equilibrium of the TGA could be

involved in the oxidation reaction at higher pH. It is possible that the pH effect on the rate of oxidation was due to the catalytic effect of OH^- (Henry et al., 1979):

$$HSCH_2COOH + OH^- \rightarrow {}^-SCH_2COOH + H_2O \quad (70.)$$

$${}^-SCH_2COOH + 2Cu^{2+} \leftrightarrow [{}^\cdot SCH_2COOH]^+ + 2Cu^+ \quad (71.)$$

$$[{}^\cdot SCH_2COOH]^+ + HSCH_2COOH \rightarrow HOOCH_2SSCH_2COOH + H^+ \quad (72.)$$

6.1.3 The elimination of metal ion catalysis in TGA oxidation

The catalysis effect of copper ions in TGA oxidation may be eliminated by the removal of the copper ions. Citric acid ($HOC_3H_4(COOH)_3$ and EDTA (ethylene diamine tetraacetic acid, $(HOOCCH_2)_2NCH_2CH_2NCH_2(COOH)_2$) can complex copper ions and are often used as inhibitors of heavy metal catalysts.

From Figure 28, it can be seen that in the acidic pH range the addition of EDTA prevented the catalytic oxidation of TGA by copper ions. However, in the pH range of 6-8, the inhibition effect of EDTA decreased rapidly with increasing pH. At pH 10 the addition of EDTA had no effect on preventing the oxidation of TGA.

Citric acid showed some inhibition effect on TGA oxidation in the presence of copper ions but it was generally much weaker than that of EDTA.

In Figure 29 the inhibition effect of CA and EDTA is shown as a function of reaction time at pH 2. As can be seen, the co-presence of $CuSO_4$ and H_2O_2 caused significant oxidation of TGA, and the amount of TGA that was left after 10 minutes of agitation was only about 30%. The addition of CA or EDTA inhibited the oxidation reaction so that the amount of TGA remaining after 10 minutes of agitation stayed at about 70-80%.

It was also observed that the catalytic effect of Fe^{3+} on the oxidation reaction of TGA is similar to that of Cu^{2+}. The inhibition of CA and EDTA on the catalytic effect of Fe^{3+} and Cu^{2+} can be seen from the stability constant of their metal complexes (Thomas, 2001):

$Fe^{2+} + CA \leftrightarrow [FeCA]^{+}$ $\log K_1=3.2$ (73.)

$Fe^{3+} + CA \leftrightarrow [FeCA]^{2+}$ $\log K_1=11.85$ (74.)

$Fe^{2+} + EDTA \leftrightarrow [FeEDTA]^{+}$ $\log K_1=14.3$ (75.)

$Fe^{3+} + EDTA \leftrightarrow [FeEDTA]^{2+}$ $\log K_1=25.7$ (76.)

$Cu^{2+} + CA \leftrightarrow [CuCA]^{+}$ $\log K_1=6.1$ (77.)

$Cu^{2+} + EDTA \leftrightarrow [CuEDTA]^{+}$ $\log K_1=18.8$ (78.)

As can be seen from above, the inhibition effect of EDTA is stronger than that of CA because the metal-EDTA complexes are more stable. In addition, the stronger depressive effect of the mixture of CA and TGA on pyrite than on chalcopyrite may be attributed to the stronger inhibition effect of CA for iron than for copper, obviously due to the higher stability of $[Fe(II)CA]^{+}$ and $[Fe(III)CA]^{2+}$ than $[CuCA]^{+}$.

6.2 Electrokinetic potential Studies

Electrokinetic potential (zeta potential) measurement is a simple in-situ technique. It detects the changes in the electrostatic charge of mineral surfaces before and after the adsorption of collectors and depressants. Researchers used it to characterize the properties of minerals and studied the influence of flotation reagents on mineral surface charges (Fuerstenau et al., 1968). Some researchers (Fornasiero et al., 1992; Fornasiero et al., 1994; Fullston et al., 1999) used this technique to systematically study the oxidation of sulfide minerals.

In this project, the influence of the different reagents on the zeta potential of minerals was studied in order to understand their adsorption on the mineral surfaces.

6.2.1 Calcite

The zeta potentials of calcite conditioned in a depressant solution, a collector solution, or first with a depressant then with a collector, are presented as a function of pH

in Figure 30. Without the addition of the reagents, the zeta potential of calcite was positive in the pH range of 7-11 with a maximum at pH 9.5, which was in agreement with the measurement by Fuerstenau et al. (1968). After the addition of the depressant, i.e., a mixture of CA and TGA, the calcite surface became negatively charged at all pH values but the zeta potential - pH curve still had the same shape as that of the calcite without the addition of any reagent. This may indicate that the adsorption density of citrate and thioglycollate anions on the calcite surface was almost constant over the pH range of 7-11. When calcite was conditioned with sodium oleate, the surface of calcite became negatively charged in the pH range of 8-12 and the minimum was in the pH range of 10-11. This indicated that oleate anions adsorbed on the surface of calcite and changed its surface charge. In the pH range of 10-11, the adsorption density of oleate anion on calcite surface was the highest.

When the calcite was treated with the mixture of CA and TGA first then with sodium oleate, the surface of calcite became more negatively charged, and the magnitude of the zeta potential was almost equal to the sum of the zeta potentials when the CA - TGA mixture and sodium oleate were added separately. This seemed to indicate that the adsorption of the depressants and the collector on calcite was not mutually exclusive. They could adsorb on the calcite surface simultaneously.

The zeta potential of calcite in the presence of CA and TGA is presented in Figure 31. After the addition of CA, calcite became strongly negatively charged. Addition of TGA also made the calcite negatively charged, but not to the same extent as CA. Interestingly, when the CA and TGA were added together, the calcite was less negatively charged than when either one was used alone. This may indicate that CA and TGA were mutually exclusive on the calcite surface, i.e., the presence of CA would reduced the adsorption of TGA, and vice versa. That is probably why the mixed depressant did not depress the flotation of calcite.

6.2.2 Dolomite

As can be seen in Figure 32, when solution pH is less than 12, the zeta potential of dolomite was positive but decreased with increasing pH. When dolomite was conditioned

in a solution of CA and TGA, its surface became strongly negatively charged. Similar to calcite, the decrease of zeta potential paralleled the curve without the mixed depressant. When dolomite was conditioned with sodium oleate, the surface of dolomite became negative below pH 10.5 and above pH 12. This may indicate that adsorption of sodium oleate on the dolomite surface was strong when pH was lower than 10.5 and higher than 12. Apparently, the adsorption of sodium oleate at the dolomite surface was not as strong as on calcite. When the mixture of CA and TGA was added and then followed by sodium oleate, the surface of dolomite became more negatively charged than when any of the reagents was used alone.

6.2.3 Pyrite

The zeta potentials of pyrite after the addition of depressant, collector, and depressant followed by collector are presented in Figure 33. Pyrite surface was positively charged below pH 12, which indicated that during the conditioning in aqueous solution its surface was oxidized to some moderate degree as predicted by some researchers (Fornasiero et al., 1992; Fornasiero et al., 1994; Fullston et al., 1999). When pyrite was conditioned in sodium oleate solution, it became strongly negatively charged in the pH range of 7-12. When the mixture of CA and TGA was added, pyrite became strongly negatively charged in the pH range of 3-12. When mixture of CA and TGA was added followed by the sodium oleate the zeta potential was similar to that when the mixture of CA and TGA was added alone. It seemed that the adsorption tendency of CA and TGA on pyrite surfaces was stronger than sodium oleate.

The interaction of CA and TGA on the pyrite surface is presented in Figure 34. As can be seen, the addition of CA drove the surface charge of the pyrite to more negative values than TGA.

6.2.4 Chalcopyrite

As can be seen in Figure 35, the zeta potential of chalcopyrite was dependent on pH. When pH was lower than 12, zeta potential decreased with increasing pH. When pH was above 12, zeta potential increased with increasing pH. The isoelectric point was 5, which

was in agreement with the measurement by other researchers (Fornasiero et al., 1992; Fornasiero et al., 1994; Fullston et al., 1999). When sodium oleate and the mixture of CA and TGA were added, chalcopyrite became more negatively charged and the zeta potential followed the same pattern as the chalcopyrite without the addition of any reagents. This may indicate that oleate and the mixture of CA and TGA adsorbed on the chalcopyrite surface through chemisorption or surface precipitation.

The interaction of CA and TGA when adsorbed on the chalcopyrite surface is presented in Figure 36. As can be seen, CA could make the chalcopyrite surface charge strongly negative, but the effect of TGA was not apparent, especially in the pH range of 8-11. In the pH range of 6-11, the zeta potential of chalcopyrite conditioned in the mixture of CA and TGA seems to fall between the values when CA and TGA were added alone.

6.3 The mechanism of interaction between reagents and sulfide mineral surfaces

Fourier transform infrared spectroscopic measurements were taken to delineate the mechanism by which reagents adsorb on mineral surfaces.

6.3.1 Adsorption of sodium oleate on sulfide mineral surfaces

The FTIR spectra of pyrite and chalcopyrite after treatment with sodium oleate at pH 10 are shown in Figure 37 and Figure 38, respectively. The absorption bands at 3050-2800 cm^{-1} are assigned to $-CH_2$ stretching (Miller & Keller, 1999; Young and Miller, 2000). The bands at 1650 -1538 cm^{-1} are attributed to the asymmetric stretching vibration of the $-COO^-$, and those at 1470 - 1360 cm^{-1} are due to the symmetric stretching vibration of the $-COO^-$ (Smith, 1999). The presence of these absorption bands indicated that oleate is adsorbed on both pyrite and chalcopyrite surfaces.

The adsorbed oleate on sulfide surfaces may have several forms: the chemisorbed form (reaction of a single oleate radial with each metal ion), a strongly bound metal dioleate (each metal ion is coordinated with two oleates) or physisorbed form due to coulombic attraction. All of them have their own characteristic absorption bands: metal

dioleate has two asymmetric absorption bands at 1650-1538, physisorbed oleate has an asymmetric absorption band at 1560 (the characteristic spectra of sodium oleate), and chemisorbed oleate has an asymmetric absorption band shifted from 1560 to lower wavenumbers due to the interaction of oleate and metal atoms. Therefore, it is possible to identify whether metal dioleate exists on the mineral surface according to the characteristic asymmetric $-COO^-$ vibration at 1538-1560 and the number of absorption peaks of asymmetric $-COO^-$ vibration.

The FTIR spectra of pyrite after treatment with sodium oleate seemed to indicate that the adsorption of oleate at the pyrite surface is not physisorption or chemisorption because the characteristic singlet of asymmetric $-COO^-$ around 1560 cm^{-1} was not observed. The characteristic doublet at 1575 cm^{-1} and 1538 cm^{-1} indicates the existence of metal dioleate.

Figure 38 shows the FTIR spectra of chalcopyrite after treatment with sodium oleate. The characteristic doublet at 1577 cm^{-1} and 1538 cm^{-1} indicated that cupric dioleate existed at the chalcopyrite surface. The low intensity of the metal dioleate bands at 1577 cm^{-1} and 1538 cm^{-1} and the high intensity of characteristic bands at 1438 cm^{-1} indicated that chemisorbed oleate may exist at the chalcopyrite surface.

6.3.2 Adsorption of TGA on the sulfide mineral surface

This infrared spectroscopic study includes a comparison of IR spectra of minerals treated by TGA with those of the corresponding metal-TGA compounds. Reaction between TGA and ferric ions did not form precipitate, so only copper-TGA precipitate was prepared and used for comparison.

6.3.2.1 Infrared spectra of reaction products between copper ions and TGA

Figure 39 shows a typical IR spectrum of the freshly prepared reaction product of TGA and $CuSO_4$, which was dried in vacuum at room temperature. Intense absorption bands from 3500 cm^{-1} to 2500 cm^{-1}, are due to -OH stretching. These spectra are around 3000 cm^{-1} and the full width at half height of these bands is 800 cm^{-1}. These bands

indicate that the –COOH group exists in the reaction products (Smith, 1998). The assignment of the absorption bands is shown in the insert table.

Figure 40 shows the IR spectrum of the reaction product of TGA and $CuSO_4$ after it was exposed to air for 12 hours. The intensity of the bands at 3500-2500 cm^{-1} became lower. Correspondingly, the product color gradually changed from yellow to black. This probably indicated that the –COOH concentration decreased significantly upon aging. The characteristic bands at 1693 cm^{-1}, 1421 cm^{-1}, 1300 cm^{-1}, 1192 cm^{-1}, 1145 cm^{-1} and 884 cm^{-1} disappeared and new bands at 1566 cm^{-1} and 1407 cm^{-1} appeared, which were the adsorption bands of the -COO^- group due to asymmetric -COO^- stretching vibration and symmetric -COO^- stretching vibration, respectively.

Figure 41 shows the IR spectrum of the product of TGA and $CuSO_4$ reaction with an excessive amount of $CuSO_4$. The spectrum is similar to that of Figure 40, but no band at 1700 cm^{-1} occurred and the bands at 1566 cm^{-1} and 1407 cm^{-1} in Figure 40 were shifted to 1571 cm^{-1} and 1381 cm^{-1} respectively. The intensity of bands at 3500-2500 cm^{-1} which were attributed to the –OH group became lower and the bands at 1650-1360 cm^{-1} which were assigned to –COO^- became stronger. This indicated that the product contains relatively more –COO^- groups.

It can be seen from Figure 39 and Figure 40 that absorption peaks of the –COOH group exist in the IR spectra of the reaction products between TGA and Cu ions and their intensities decreased with aging. These probably indicated that at the beginning, copper ions reacted only with –SH groups and did not react with –COOH groups when forming a copper–TGA salt. During aging (probably oxidation as well), the linkage between Cu and S in the TGA structure is broken and Cu reacted with the –COOH group. The breakage of bonding between Cu and S may be due to dimer formation from TGA in which –COOH groups became –COO^- groups.

6.3.2.2 Infrared spectra of pyrite and chalcopyrite after treatment with TGA

The spectra of pyrite after treatment with TGA at pH 2 and pH 10 are showed in Figure 42 and Figure 43, respectively. As can be seen, there are no characteristic

absorption bands of TGA on pyrite at either pH 2 or pH 10. Apparently, no TGA adsorbed on the pyrite surfaces.

The spectrum of chalcopyrite after treatment with TGA at pH 2 and pH 10 are shown in Figure 44 and Figure 45, respectively. Compared to the spectra of products of TGA-Cu reaction (Cu overdosage, Figure 41), the disappearance of the characteristic doublet at 1571 cm^{-1} and 1381 cm^{-1} and the occurrence of characteristic singlet at 1446 cm^{-1} indicate the chemisorption of TGA on the chalcopyrite surface: the shift of the band to 1446 cm^{-1} may be attributed to the asymmetric stretching vibration of the $-COO^-$ by the interaction between Cu and the $-COO^-$ group. The band at 877 cm^{-1} is due to the out of plane –OH bending vibration. Combined with the disappearance of the –COOH group, it is concluded that TGA was adsorbed on the chalcopyrite surface through the COO^- groups or through a chelate of COO^- group and –SC- groups. This will be discussed in the next section.

pH had a marked effect on the adsorption of TGA on the mineral surfaces. As can be seen from Figure 45 and Figure 44, TGA adsorbed on the chalcopyrite surface at pH 10 but not at pH 2.

6.3.2.3 Configuration of adsorption TGA on chalcopyrite surfaces

When metal ions are reacted with TGA to form a salt, bonding could occur through either the mercapto group or the carboxyl group because both of them are chemically reactive (Liu, 1985). From the infrared spectroscopic studies, it is seen that TGA adsorbed on the chalcopyrite surfaces by the COO^- groups or a chelate of COO^- group and –SC– groups. This is illustrated in Figure 46.

Even though the characteristic bands of S-S at 540-505 cm^{-1} were not observed clearly, DTGA adsorption on the chalcopyrite surfaces by either one or both of $-COO^-$ groups is also possible because the copper ions could catalyze the oxidation of TGA to DTGA and one or two of the –COOH groups in DTGA may dissociate and react with Cu. The schematic diagram of DTGA on chalcopyrite surface is presented in Figure 47.

However, bonding between Cu and –S-C– could also take place. It was shown earlier that TGA-Cu salt was first formed as Cu-S-C– bonding and then part of it was converted to –COO–Cu bonding. It is speculated that at the beginning TGA adsorbed on the chalcopyrite surface mainly by the –S–C– bonding with some $-COO^-$ bonding. Then because of oxidation, which could be catalyzed by an overdose of Cu ions, only $-COO^-$ remained bonded on the chalcopyrite surface while the Cu–S–C– bonds were broken to form the DTGA dimers. The initial stage of the adsorption may appear as shown in Figure 48.

In addition, it was observed that the different reaction products of TGA and Cu could be changed reversibly. When TGA was added continuously to a $CuSO_4$ solution so as to cause a TGA overdosage, the precipitate changed from black to yellow. When more Cu ions were then added to this system or when the resulting products were aged, the yellow precipitate became black again. Therefore, multiple forms of TGA on the chalcopyrite surfaces were possible under different conditions.

However, the hydrophilic characters of these adsorption forms are different. The configuration shown in Figure 48 is the most effective because the adsorption layer can form hydrogen bonds with H_2O and make the chalcopyrite strongly hydrophilic. The structure in Figure 47 is the worst for the dimer of TGA as the exposed S–S bonds may render mineral surfaces hydrophobic. Because oxidation would cause the change of bonded Cu–S– to Cu–COO which was the less effective form in terms of surface hydrophilicity, and because the addition of CA hindered the conversion, the depressive effects of TGA would be increased when it was used together with CA.

6.3.3 Depression mechanism of TGA on sulfide minerals with sodium oleate as a collector

6.3.3.1 Interaction of TGA with NaOl on pyrite surface

Figure 49 presents the FTIR spectrum of pyrite after conditioning with TGA followed by NaOl at pH 10. The band at 1560 cm^{-1} is due to asymmetric $-COO^-$ vibration of sodium oleate, and the bands at 1463, 1446, and 1425 cm^{-1} are due to symmetric $-COO^-$

vibration of sodium oleate. This suggested that sodium oleate probably existed in its original form on the pyrite surface.

Compared with the spectrum of pyrite conditioned with NaOl (in Figure 37), it is noticed that the characteristic doublet bands at 1574 cm^{-1} and 1538 cm^{-1}, which indicated the metal dioleate of NaOl on the pyrite surface, disappeared after the pyrite was pretreated with TGA. This suggested that the presence of TGA prevented the formation of metal dioleate on the pyrite surface.

As discussed earlier, TGA did not adsorb on the pyrite surface. The prevention of NaOl adsorption on the pyrite surface by TGA may be illustrated by the following:

- Pyrite oxidizes to form an iron hydroxyl as the initial oxidation products at the surface of pyrite:

$$FeS_2\vert\ FeS_2 + OH^- + 4O_2 + e^- \ ?\ \ FeS_2\vert\ Fe(OH)^{2+} + 2SO_4^{2-} \qquad (79.)$$

$$FeS_2\vert\ FeS_2 + 2OH^- + 4O_2 + e^- \ ?\ \ FeS_2\vert\ Fe(OH)_2^{+} + 2SO_4^{2-} \qquad (80.)$$

- Oleate groups then adsorb on the positively charge oxidation products via coulombic attraction to form an iron hydroxyl oleate on the surface:

$$FeS_2\vert\ Fe(OH)^{2+} + Ol^- \ ?\ \ FeS_2\vert\ Fe(OH)Ol_2 \qquad (81.)$$

$$FeS_2\vert\ Fe(OH)_2^{+} + Ol^- \ ?\ \ FeS_2\vert\ Fe(OH)_2Ol \qquad (82.)$$

- Formation of multiple layers of metal dioleate precipitate on the pyrite surface using reagent-covered surface as nucleus.

$$FeS_2\vert\ Fe(OH)Ol_2 + Fe^{2+} + Ol^- \ ?\ \ FeS_2\vert\ Fe(OH)Ol_2\ Fe(Ol)_2 \qquad (83.)$$

$$FeS_2\vert\ Fe(OH)_2Ol + Fe^{2+} + Ol^- \ ?\ \ FeS_2\vert\ Fe(OH)_2Ol\ Fe(Ol)_2 \qquad (84.)$$

It is known that metal dioleate precipitates at the mineral surface induce hydrophobicity.

- TGA prevents the adsorption of Ol^- on the pyrite surface by preventing the formation of positive species such as $Fe(OH)^{2+}$ or $Fe(OH)_2^+$. This is because TGA can form soluble complexes with Fe^{2+} or Fe^{3+} formed on the surface of pyrite during oxidation. This can be illustrated as follows:

$$FeS_2|\ Fe(OH)^{2+} + 3[TGA]^{-1} \ ?\ \ FeS_2|\ OH^- + Fe[TGA]_3 \qquad (85.)$$

$$FeS_2|\ Fe(OH)_2^+ + 3[TGA]^{-1} \ ?\ \ FeS_2|\ (OH^-)_2 + Fe[TGA]_3 \qquad (86.)$$

However, small amounts of oleate may still adsorb on the pyrite surface due to the large amount of iron hydroxides formed as a results of aggressive oxidation of the mineral.

Sulfide minerals are insoluble so that it is difficult for TGA to complex with the lattice metal ions. When the mineral is oxidized, the oxidation products, typically metal hydroxide, are more readily complexed by TGA and removed from the surface.

6.3.3.2 TGA and NaOl interaction on chalcopyrite surfaces

Figure 50 presents the FTIR spectra of chalcopyrite after conditioning with TGA followed by NaOl at pH 10. The band at 1555 cm^{-1} indicated the chemisorption of the $-COO^-$ group in TGA onto chalcopyrite. The shift of this band from 1446 to 1555 cm^{-1} may be due to the influence of oleate on the interaction between oleate and copper atoms. The bands at 1560 cm^{-1} is due to asymmetric $-COO^-$ vibration of sodium oleate, and the bands at 1463, 1446, and 1425 cm^{-1} are due to symmetric $-COO^-$ vibration of sodium oleate. This suggested that sodium oleate also existed in its original form on the chalcopyrite surface. In addition, bands attributed to $-CH_2$ stretching at 3050 - 2800 cm^{-1} were very strong.

Compared with the spectrum of chalcopyrite conditioned with NaOl (in Figure 38), it is noticed that the characteristic doublet bands at 1578 cm^{-1} and 1583 cm^{-1} which indicate the formation of metal dioleate on the chalcopyrite surface disappeared after it was pretreated with TGA. The characteristic singlet band at 1439 cm^{-1} which may be due to the chemisorption of NaOl on chalcopyrite also disappeared. These observations

suggested that the presence of TGA prevented formation of metal dioleate and the chemisorption of oleate on the chalcopyrite surface. Sodium oleate can only exist in its original form on the chalcopyrite surface, but due to chemisorption of TGA the chalcopyrite surface is hydrophilic.

The prevention of NaOl adsorption on the chalcopyrite surface by TGA may be illustrated by the following:

- Chalcopyrite oxidizes to form an iron hydroxyl, similar to the initial oxidation products at the surface of pyrite:

$$CuFeS_2\,|\,CuFeS_2 + 2OH^- + 4O_2 + 2e^- \;?\; CuFeS_2\,|\,CuFe(OH)_2 + 2SO_4^{2-} \qquad (87.)$$

- Oleate groups adsorb on the chalcopyrite surface:

$$CuFeS_2\,|\,CuFe(OH)_2 + 2Ol^- \;?\; CuFeS_2\,|\,CuFeOl_2 + 2OH^- \qquad (88.)$$

- Formation of metal dioleate precipitate on the chalcopyrite surface through reagent-covered surface as nucleus.

$$CuFeS_2\,|\,CuFeOl_2 + Cu^{2+} + Fe^{2+} + 4Ol^- \;?\; CuFeS_2\,|\,CuFeOl_2Cu(Ol)_2Fe(Ol)_2 \qquad (89.)$$

- TGA prevents the adsorption of Ol^- on the chalcopyrite surface through the chemisorption of TGA on the chalcopyrite surface. This can be illustrated as follows:

$$CuFeS_2\,|\,CuFe(OH)_2 + 2[TGA]^{-1} \;?\; CuFeS_2\,|\,CuFe(TGA)_2 + 2OH^- \qquad (90.)$$

6.3.4 Summary of adsorption mechanisms:

- Adsorption of oleate at the pyrite surface was through metal dioleate precipitation that may be induced by physisorption of oleate due to coulombic attraction. In contrast, occurrence of metal dioleate precipitation on chalcopyrite surface may be induced by the chemisorbed oleate monolayer.

- –SH groups have higher affinity to bond with copper ions than –COOH groups. Only when the –SH group is oxidized or exhausted then the –COOH group can react with copper ions.

- No TGA adsorbs on the pyrite surface. TGA adsorbs on the chalcopyrite surface by chemisorption. This adsorption can only take place at higher pH values.

- The adsorbed TGA on the chalcopyrite surface may have different configurations either as TGA or DTGA bonded to chalcopyrite surfaces by the –S-C- group, -COO^- group, or their chelation bonds. Among them, the bonding by the -S-C- group is the most effective way to make the chalcopyrite hydrophilic.

- The presence of TGA can prevent the adsorption of oleate on the pyrite surface by dissolving the iron ionic species from the pyrite surface. The adsorption of TGA on the chalcopyrite surface prevents the occurrence of metal dioleate and the chemisorption of oleate if it exists on the chalcopyrite surface.

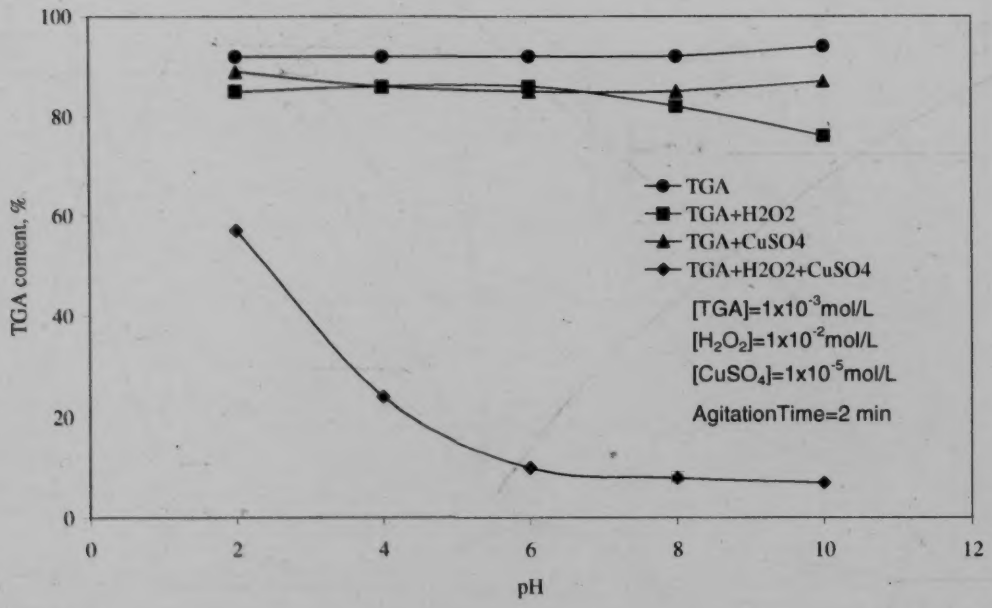


Figure 26 Catalysis effect of copper ions on TGA oxidation at different pH values

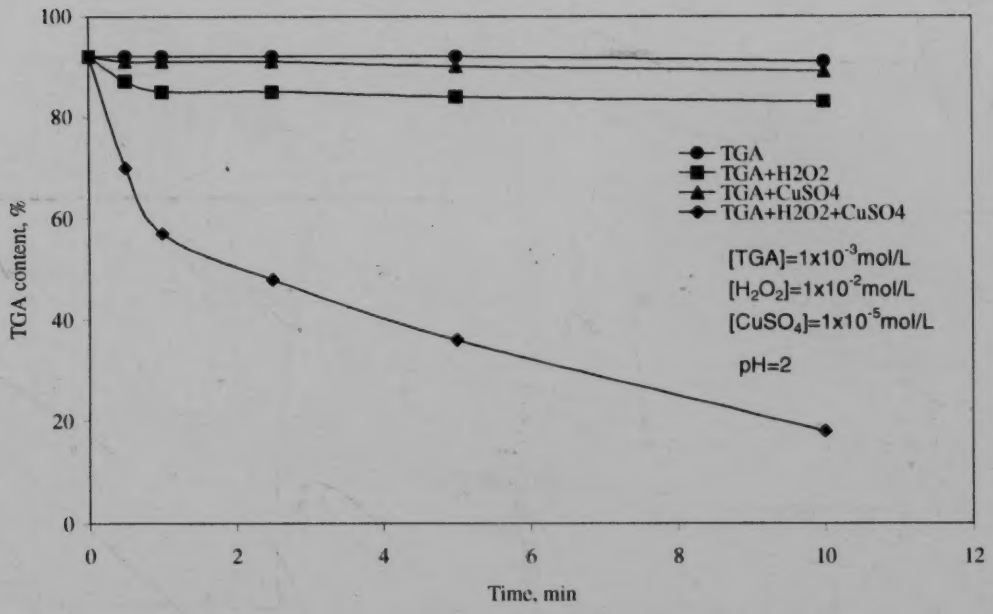


Figure 27 Catalysis effect of copper ions on the TGA oxidation with different agitation time.

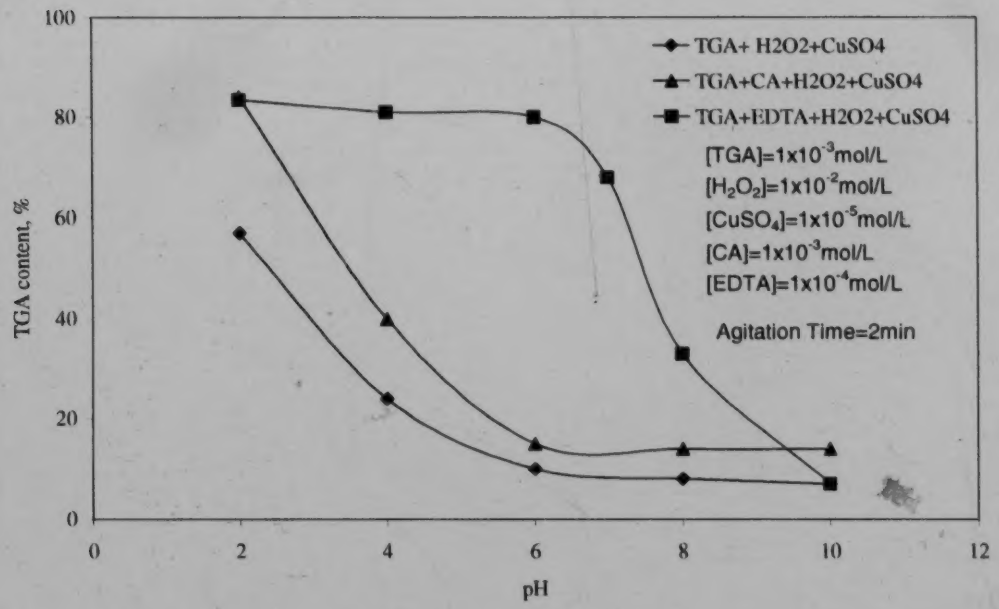


Figure 28 Inhibition effect of CA and EDTA on the Cu catalysis of TGA oxidation at different pH values

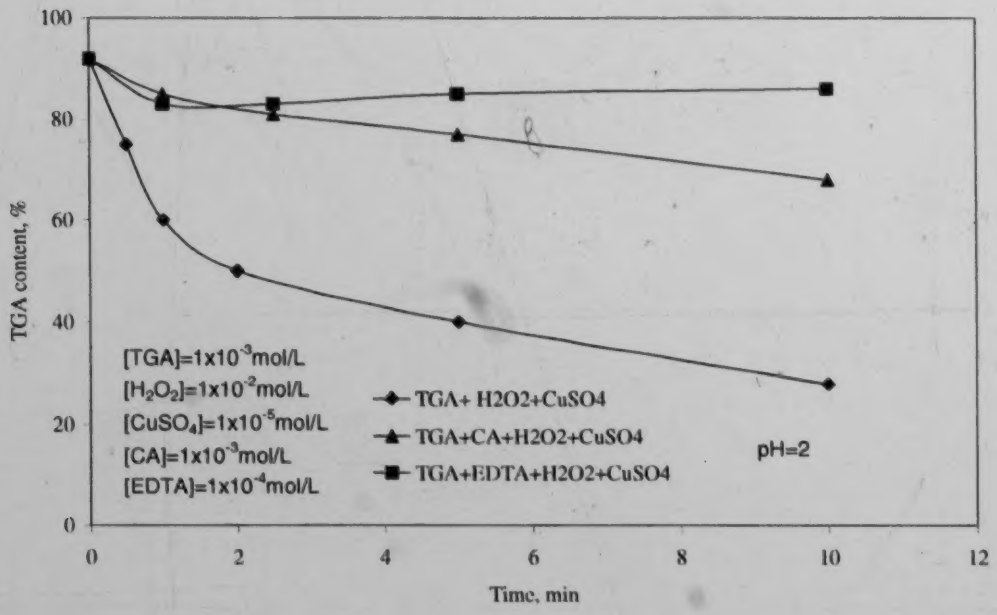


Figure 29 Inhibition effect of CA and EDTA on copper ions catalysis of TGA oxidation with different agitation time.

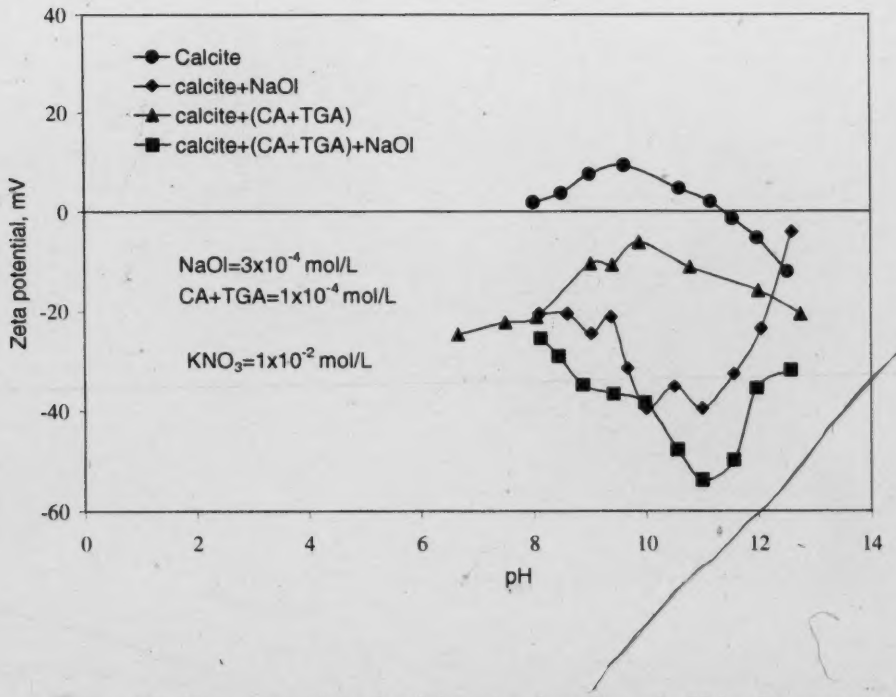


Figure 30 Zeta potential of calcite as a function of pH in the presence of depressant, collector and depressant followed by collector.

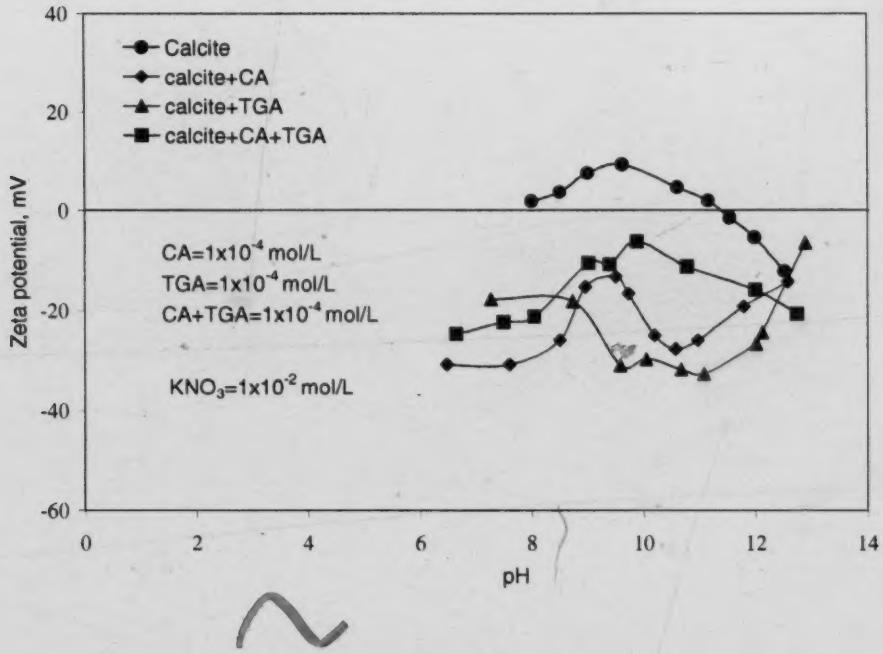


Figure 31 Zeta potential of calcite as a function of pH in the presence of CA, TGA and mixture of CA and TGA.

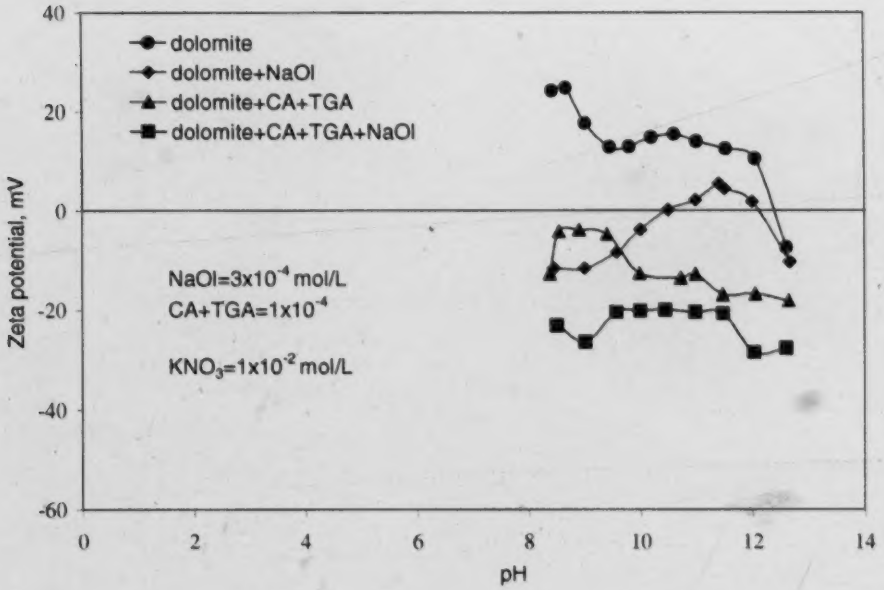


Figure 32 Zeta potential of dolomite as a function of pH in the presence of depressant, collector and depressant followed by collector.

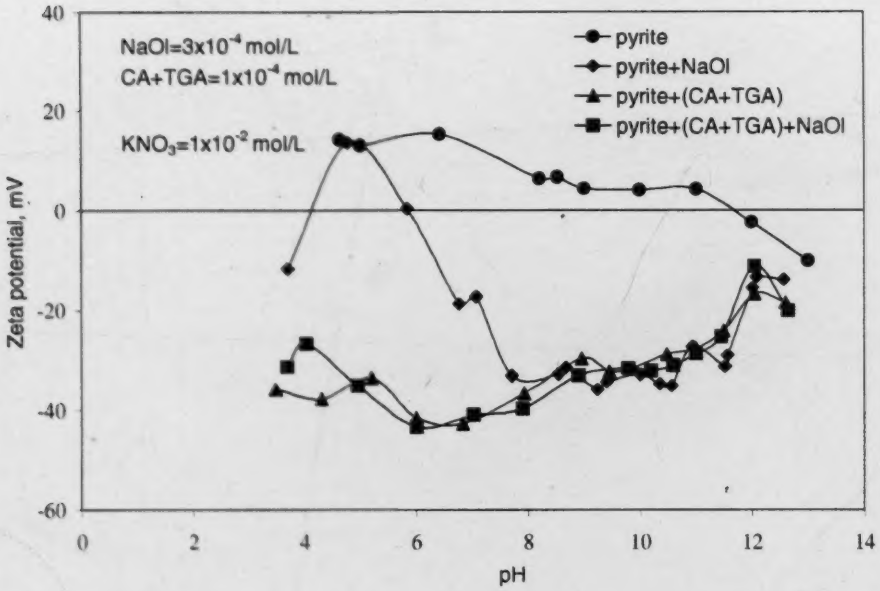


Figure 33 Zeta potential of pyrite as a function of pH in the presence of depressant, collector and depressant followed by collector.

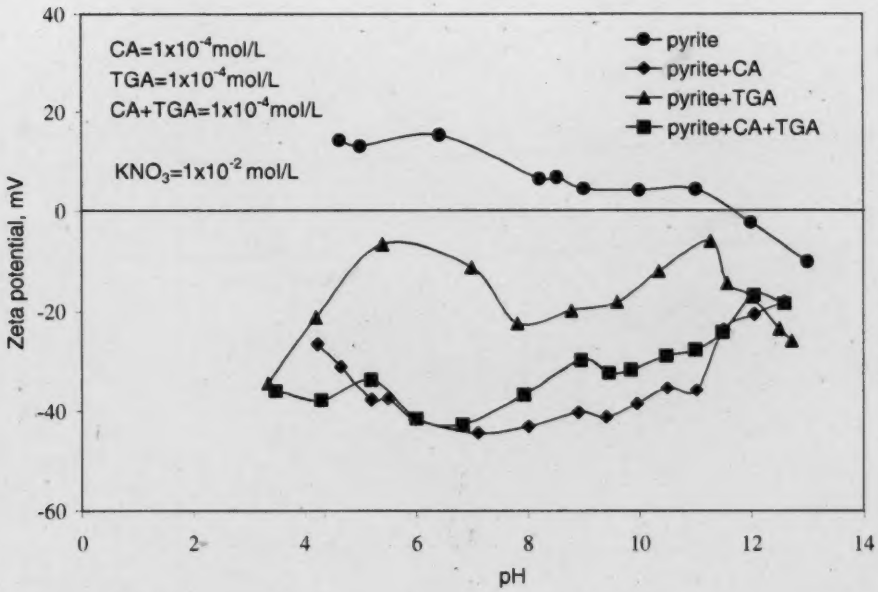


Figure 34 Zeta potential of pyrite as a function of pH in the presence of CA, TGA and mixture of CA and TGA

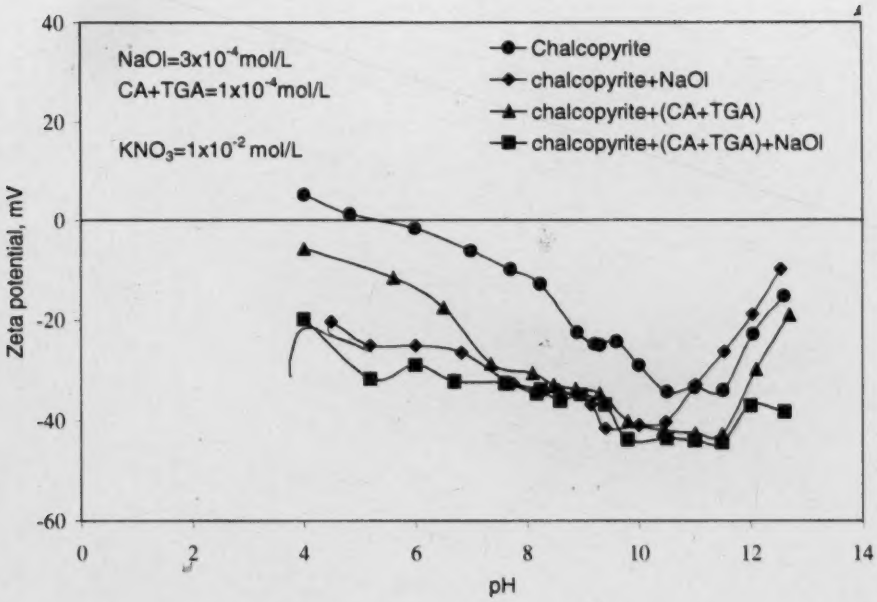


Figure 35 Zeta potential of chalcopyrite as a function of pH in the presence of depressant, collector and depressant followed by collector.

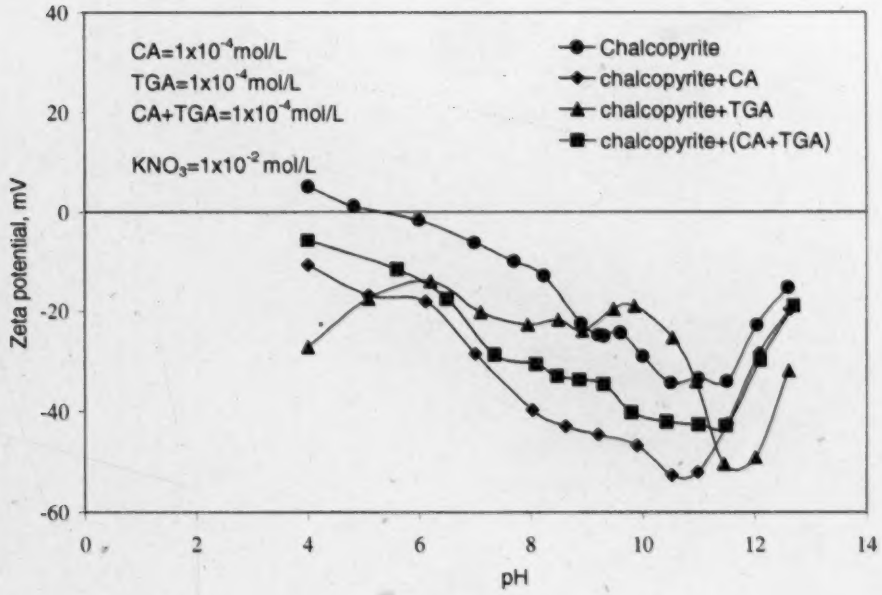
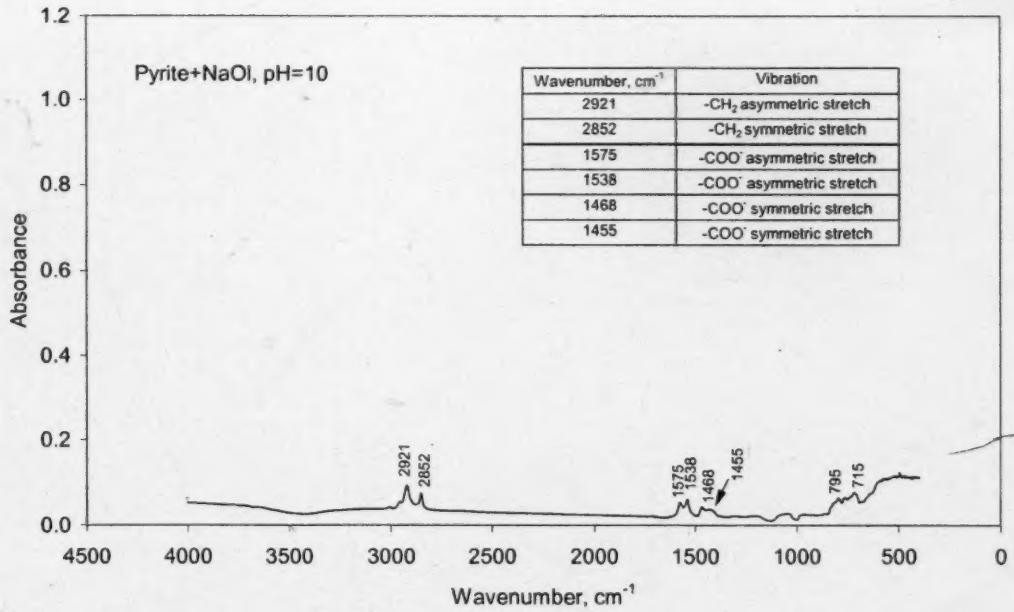


Figure 36 Zeta potential of chalcopyrite as a function of pH in the presence of CA, TGA and mixture of CA and TGA.



Wavenumber, cm^{-1}	Vibration
2921	$-CH_2$ asymmetric stretch
2852	$-CH_2$ symmetric stretch
1575	$-COO^-$ asymmetric stretch
1538	$-COO^-$ asymmetric stretch
1468	$-COO^-$ symmetric stretch
1455	$-COO^-$ symmetric stretch

Figure 37 FTIR spectrum of pyrite treated with NaOl at pH 10

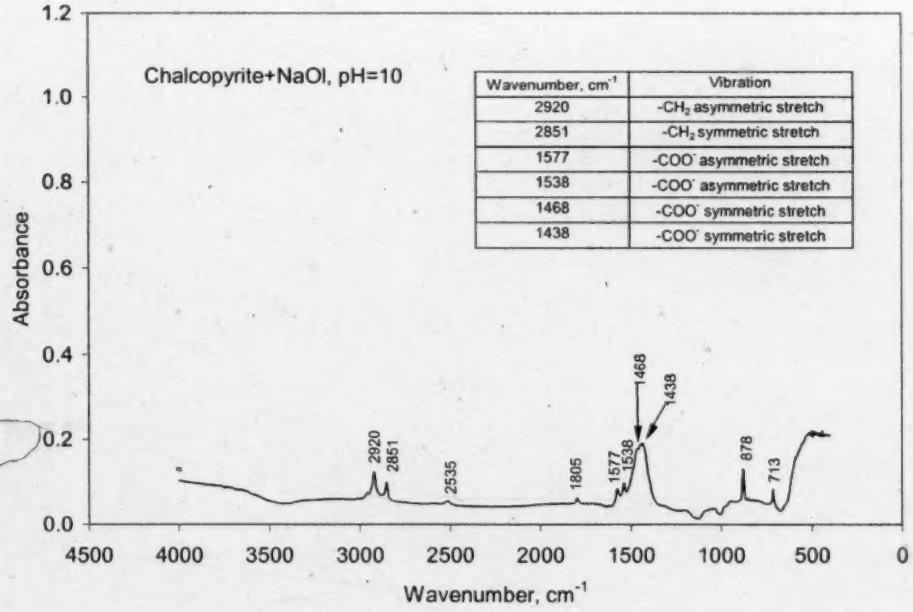


Figure 38 FTIR spectrum of chalcopyrite treated with NaOl

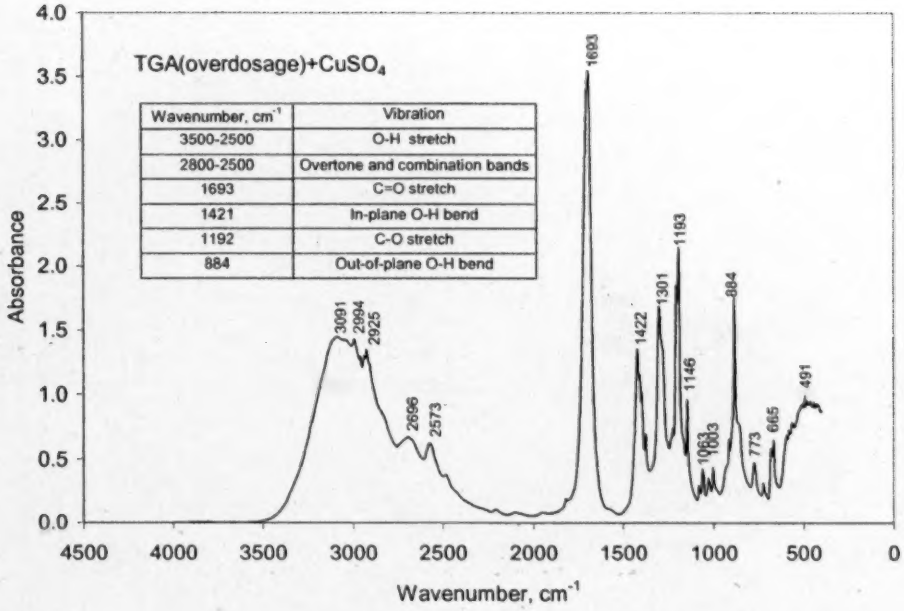


Figure 39 FTIR spectrum of freshly prepared reaction product of $CuSO_4$ and TGA

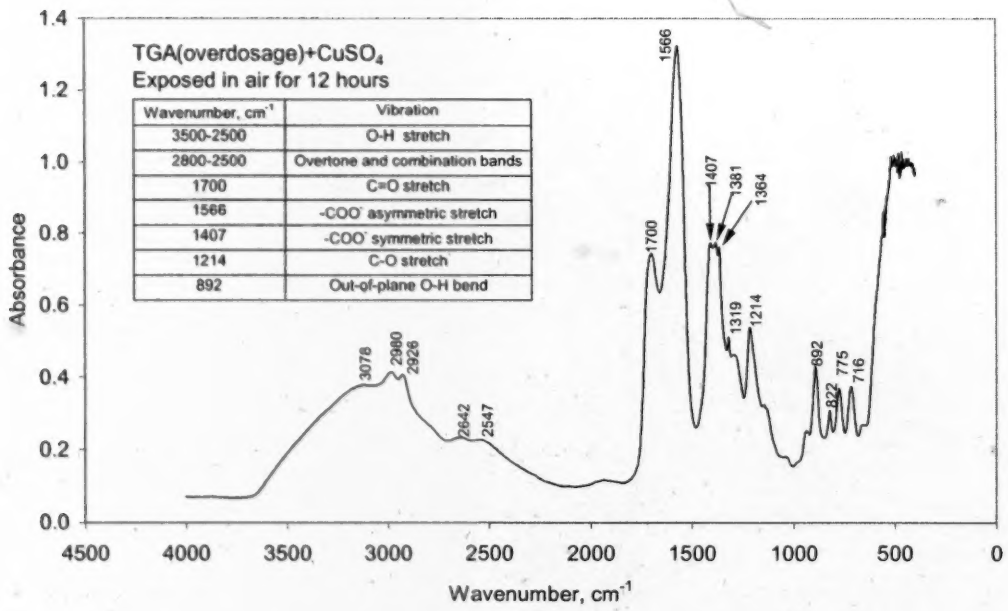


Figure 40 FTIR spectrum of reaction product of $CuSO_4$ and TGA at pH 10 exposed in air for 12 hours

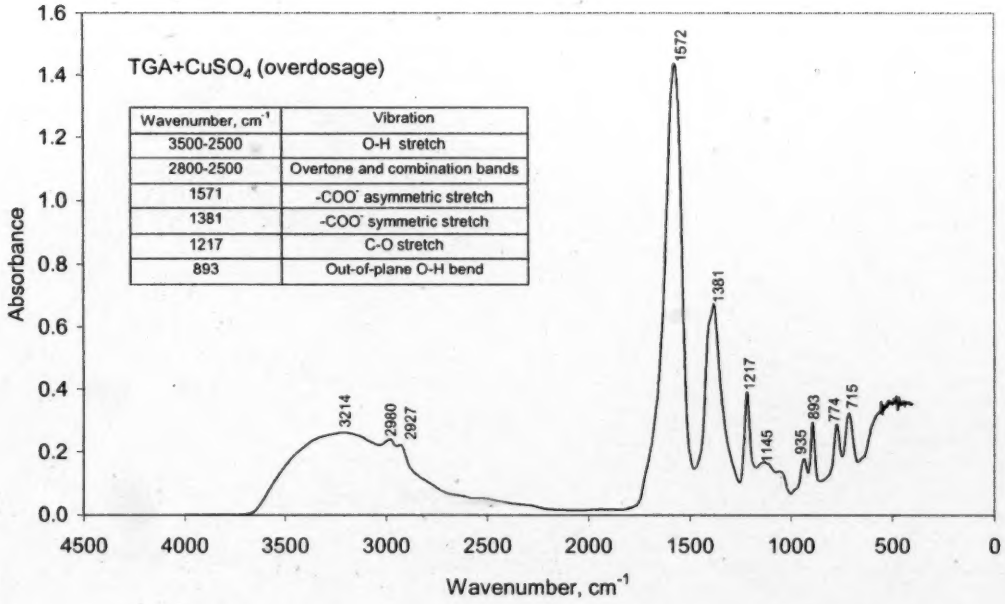


Figure 41 FTIR spectrum of reaction product of $CuSO_4$ and TGA at pH 10 when Cu ions were overdosed

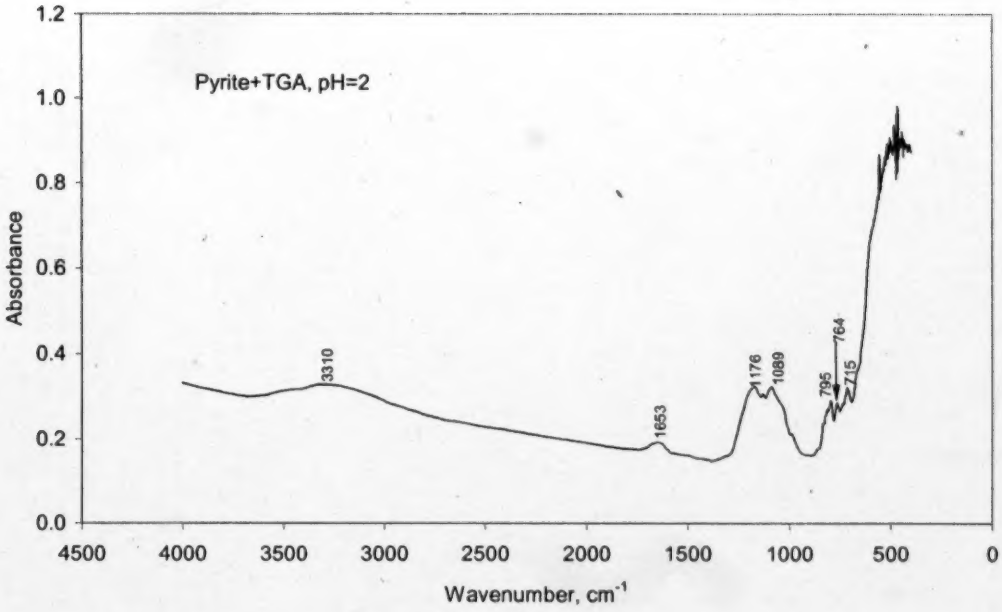


Figure 42 FTIR spectrum of pyrite treated with TGA at pH 2

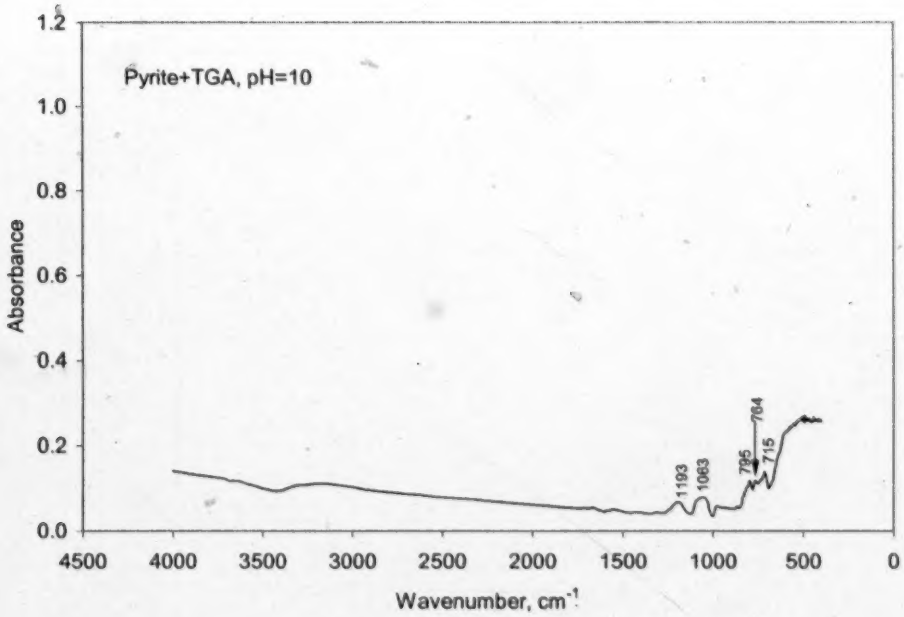


Figure 43 FTIR spectrum of pyrite treated with TGA at pH 10

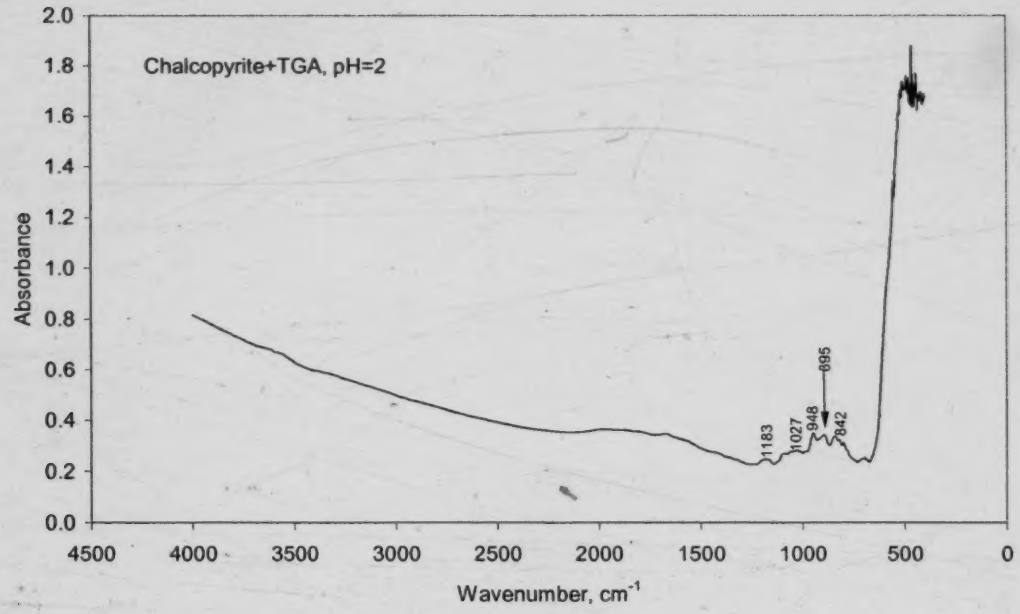


Figure 44 FTIR spectrum of chalcopyrite treated with TGA at pH 2

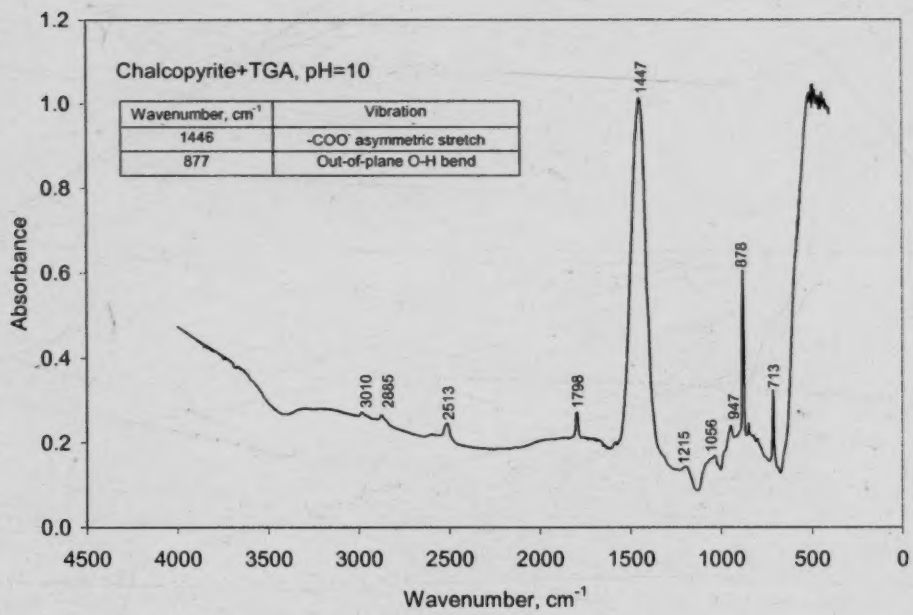


Figure 45 FTIR spectrum of chalcopyrite treated with TGA at pH 10

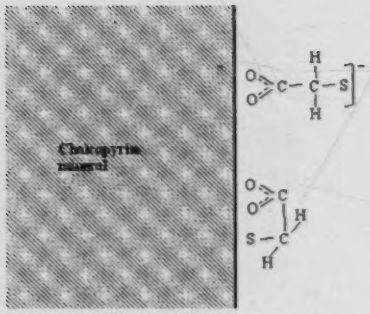


Figure 46 Schematic diagram of adsorption model of TGA onto chalcopyrite

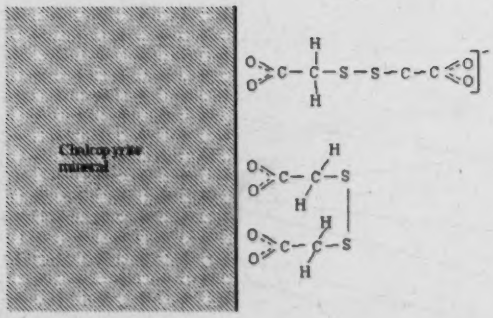


Figure 47 Schematic diagram of the adsorption model of DTGA onto chalcopyrite

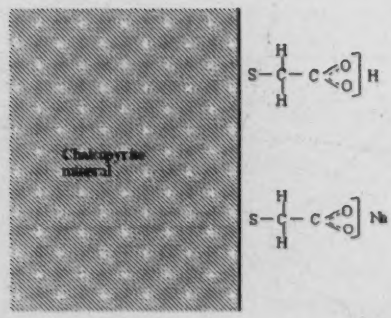
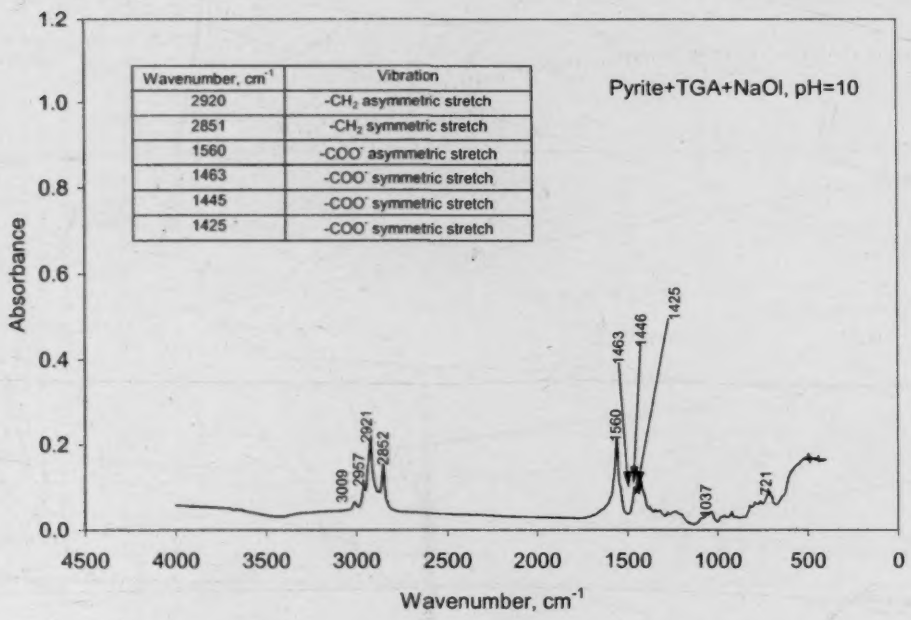


Figure 48 Schematic diagram of the adsorption model of TGA onto chalcopyrite by –S–C– group



Wavenumber, cm^{-1}	Vibration
2920	$-CH_2$ asymmetric stretch
2851	$-CH_2$ symmetric stretch
1560	$-COO^-$ asymmetric stretch
1463	$-COO^-$ symmetric stretch
1445	$-COO^-$ symmetric stretch
1425	$-COO^-$ symmetric stretch

Figure 49 FTIR spectrum of pyrite pretreated with TGA and followed by NaOl at pH 10

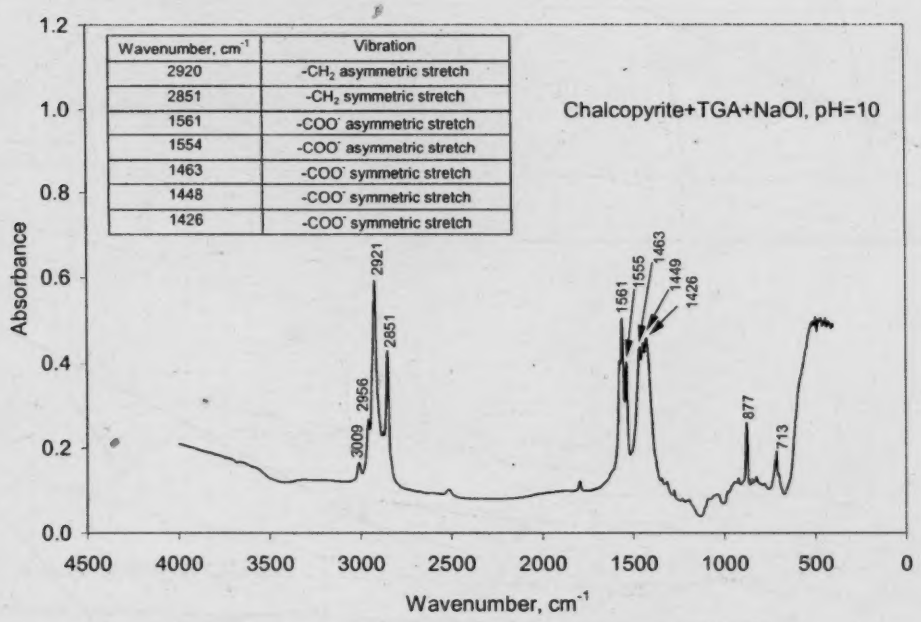


Figure 50 FTIR spectrum of chalcopyrite pretreated with TGA and followed by NaOl at pH 10

7 CONCLUSIONS

This research project was carried out with the objective of removing carbonate minerals from refractory gold-bearing sulfide ores by froth flotation. Microflotation tests were conducted on representative single minerals of carbonate such as calcite and dolomite, sulfide such as pyrite and chalcopyrite, and their mixtures, using sodium oleate as a collector and several organic chemicals as depressants.

The mechanism by which the flotation reagents functioned was studied using solution chemistry, electrokinetic potential, and fourier transform infrared spectroscopic studies. The following conclusions could be drawn from this work:

- The tested carbonate and sulfide minerals had similar floatabilities using sodium oleate as a collector, and unlike the system where xanthate was used as a collector, their separation could not be realized by raising pH to depress the sulfide minerals.
- Both thioglycollic acid (TGA) and citric acid (CA) selectively depressed the NaOl flotation of pyrite between pH 9.0 and 10.5 without affecting the flotation of calcite and dolomite. However, neither acid could depress chalcopyrite.
- When thioglycollic acid and citric acid were mixed at 1:1 molar ratio, the mixture became a much stronger selective depressant. Not only were the dosages required for pyrite depression significantly reduced, but the mixed depressant also depressed chalcopyrite, without affecting the flotation of calcite and dolomite.
- Using the mixed depressant, calcite and dolomite could be selectively floated from various artificial mineral mixtures. Generally, the separation of calcite presented no difficulty whether it was floated from pyrite or chalcopyrite. However, flotation separation of dolomite was more troublesome and mixtures of dolomite-chalcopyrite could not be separated by sodium oleate flotation using TGA and CA as depressants.
- Electrokinetic potential studies on mineral surfaces indicated that the adsorption of oleate on the pyrite surface may be through coulombic attraction while its adsorption

on the chalcopyrite surface may be through chemisorption. Chemisorption of mixtures of CA and TGA seems to prevent the adsorption of oleate on the sulfide minerals but cannot prevent its adsorption on the surface of the carbonate minerals. Combined use of CA and TGA seems to increase the adsorption of TGA on the chalcopyrite surface and decrease its adsorption on the surfaces of calcite (pH range of 8 to 12) and dolomite (pH range of 8 to 10.5).

- The different behavior of TGA as depressant to pyrite and chalcopyrite may come from the fact that TGA can be easily oxidized to its dimer by the catalytic action of copper ions and hydroxyl ions. The dimers have poor hydrophilic properties. The addition of CA may inhibit the catalytic effect of the metal ions in the oxidation of TGA to DTGA.

- Adsorption of oleate at the pyrite surface may be physisorption due to coulombic attraction, followed by metal dioleate precipitation. In contrast, adsorption of oleate on the chalcopyrite surface may be chemisorption, followed by metal dioleate precipitation.

- –SH group has a higher affinity to bond with copper ions than –COOH group because only when the –SH group is oxidized or exhausted then the –COOH group can react with copper ions.

- No TGA adsorbs on the pyrite surface. TGA adsorbs on the chalcopyrite surface by chemisorption. This adsorption can only take place at high pH values. The adsorbed TGA on the chalcopyrite surface may have different configurations either as TGA or DTGA bonded to chalcopyrite surfaces by the –S-C- group, -COO^- group, or their chelation bonds. Among them, the bonding by the -S-C- group is the most effective to make the chalcopyrite hydrophilic.

- The presence of TGA can prevent the adsorption of oleate on the pyrite surface by dissolving the iron ionic species from the pyrite surfaces. The adsorption of TGA on chalcopyrite surfaces prevents the occurrence of metal dioleate and chemisorption of oleate if it exists on the chalcopyrite surfaces.

8 RECOMMENDATIONS FOR FURTHER WORK

In this research using sodium oleate as collector and mixture of thioglycollic acid and citric acid as depressant, calcite could be separated from pyrite and chalcopyrite. However, dolomite was more troublesome and mixture of dolomite-chalcopyrite could not be separated successfully. Therefore, Intensification of process conditions for dolomite and chalcopyrite separation need to be further studied.

In addition, the flotation behavior of gold under reagent scheme used is not studied. Even though gold could be recovered with subsequent processes, the control of gold reported into float or tailing could optimize the whole gold extraction process. Therefore, flotation of gold using sodium oleate as collector and mixture of TGA and CA as depressant should be studied.

Finally, the tests of single mineral flotation and separation of mixture of single minerals prove the feasibility of proposed reverse flotation of carbonate from sulfide. In order to testify the effectiveness of its practical application, the real life refractory gold ores need to be conducted using bench flotation machines.

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